7 Derivation of the effective Hamiltonian

7.1. Introduction

The Born–Oppenheimer approximation [1] is an important linch pin in the description of molecular energy levels. It reveals the difference between electronic and nuclear motions in a molecule, as a result of which we expect the separation between different electronic states to be much larger than that between vibrational levels within an electronic state. An extension of these ideas shows that the separation between vibrational levels is correspondingly larger than the separation between the rotational levels of a molecule. We thus have a hierarchy of energy levels which reveals itself in the electronic, vibrational and rotational structure of molecular spectra. This gradation in the magnitude of the different types of quanta also provides the inspiration for an energy operator known as the effective Hamiltonian.

In this chapter we introduce and derive the effective Hamiltonian for a diatomic molecule. The effective Hamiltonian operates only within the levels (rotational, spin and hyperfine) of a single vibrational level of the particular electronic state of interest. It is derived from the full Hamiltonian described in the previous chapters by absorbing the effects of off-diagonal matrix elements, which link the vibronic level of interest to other vibrational and electronic states, by a perturbation procedure. It has the same eigenvalues as the full Hamiltonian, at least to within some prescribed accuracy.

The motivation for constructing the effective Hamiltonian is one of economy and perhaps even of feasibility. It reproduces the eigenstates of the vibronic state of interest but with a much smaller representation than that of the full Hamiltonian. The effective Hamiltonian provides a natural resting point in the journey from experiment to theory. It permits data to be fitted in an unprejudiced fashion, the parameters being determined by statistical criteria only. These parameters in turn can be interpreted in terms of various theoretical models for the electronic states, and provide a point of comparison for *ab initio* calculations. A soundly based effective Hamiltonian makes allowance for all possible admixtures of electronic states; the relative importance of the perturbations by these different states is determined by a detailed comparison of the parameter values with theoretical predictions. In this way, the task of data fitting is clearly separated from that of theoretical interpretation.

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It took several decades for the effective Hamiltonian to evolve to its modern form. It will come as no surprise to learn that Van Vleck played an important part in this development; for example, he was the first to describe the form of the operator for a polyatomic molecule with quantised orbital angular momentum [2]. The present formulation owes much to the derivation of the effective spin Hamiltonian by Pryce [3] and Griffith [4]. Miller published a pivotal paper in 1969 [5] in which he built on these ideas to show how a general effective Hamiltonian for a diatomic molecule can be constructed. He has applied his approach in a number of specific situations, for example, to the description of N_2 in its $A\ ^3\Sigma_u^+$ state [6], described in chapter 8. In this book, we follow the treatment of Brown, Colbourn, Watson and Wayne [7], except that we incorporate spherical tensor methods where advantageous. It is a strange fact that the standard form of the effective Hamiltonian for a polyatomic molecule [2] was established many years before that for a diatomic molecule [7].

7.2. Derivation of the effective Hamiltonian by degenerate perturbation theory: general principles

We commence with some groundwork which will enable us to define the problem and state our ultimate goal. Although the method we present in this section is completely general for systems with discrete eigenstates, consideration of a particular example is often a helpful way of appreciating the principles involved. With this in mind, we shall exemplify points in this section by outlining how the method may be applied to derive an effective Hamiltonian which operates entirely within a given vibronic state. The actual details of how the method can be applied to this as well as the other cases of interest are given later in this chapter.

It is always possible to divide the total Hamiltonian $\mathcal{H}$ into a major part $\mathcal{H}^0$ (the zeroth-order Hamiltonian) and a perturbation $\lambda\mathcal{H}'$:

$$\mathcal{H} = \mathcal{H}^0 + \lambda\mathcal{H}', \tag{7.1}$$

where λ is a dimensionless parameter in the range $0 \leq \lambda \leq 1$. Thus, for example, in the derivation of an effective Hamiltonian operating in a particular vibronic state, $\mathcal{H}^0$ might be comprised of the non-relativistic electronic kinetic energy operators, the vibrational kinetic energy and the electrostatic potential terms; $\lambda\mathcal{H}'$ would then be composed of all the remaining terms in the total Hamiltonian. It is now helpful to introduce two different sorts of quantum number. The first sort, which we denote in general by η, label the distinct eigenstates of the zeroth-order Hamiltonian; each of these eigenstates is g_η-fold degenerate. In our particular example, η would represent the quantum numbers required to specify a particular vibronic state; the energy separation between these states is typically between 10^3 and 10^4 cm^{-1}. Following a well-established convention, the lowest of these vibronic states (the ground state) is labelled $|0\rangle$. The second sort of quantum number, denoted in general by i, identifies the individual substates in a particular state η. In our example, i would represent the rotational, electron spin and nuclear spin quantum numbers. Substates distinguished by different i are, of course,

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degenerate in the solution of $\mathcal{H}^0$. However, there are perturbing terms in the Hamiltonian which connect different vibronic states. These terms lift the degeneracy of some or all of the g_η states by amounts which are typically around 1 cm^{-1}. Although these terms in $\lambda\mathcal{H}'$ are usually small compared with the separation of different vibronic states, their effects can dominate high-resolution microwave or radiofrequency spectra.

Next, we show how these two types of quantum number are used to label the eigenstates involved. The zeroth-order eigenstates and eigenvalues are defined by

$$\mathcal{H}^0|0, i\rangle^0 = E_0^0|0, i\rangle^0, \tag{7.2}$$

$$\vdots$$

$$\mathcal{H}^0|\eta, i\rangle^0 = E_\eta^0|\eta, i\rangle^0, \tag{7.3}$$

$$\vdots$$

We note that each of these equations actually represents g_η equations, corresponding to the g_η distinct values of i in each state, η. These g_η functions $|\eta, i\rangle^0$ are, for convenience, chosen to be orthonormal to each other, that is,

$${}^0\langle\eta, i \mid \eta, j\rangle^0 = \delta_{ij}. \tag{7.4}$$

In addition, the functions $|\eta, i\rangle^0$ define what is called a g_η-fold subspace of total Hilbert space. Furthermore, the eigenfunctions of two states with different values of η must be orthogonal since $\mathcal{H}^0$ is a Hermitian operator. Once again we normalise these functions to unity so that (7.4) may be generalised to

$${}^0\langle\eta, i \mid \eta', j\rangle^0 = \delta_{\eta\eta'}\delta_{ij}. \tag{7.5}$$

Thus the members of the orthonormal set $|\eta, i\rangle^0$ are all orthogonal to those of the orthonormal set $|\eta', j\rangle^0$ for $\eta' \neq \eta$; correspondingly the subspaces defined by these two sets are said to be orthogonal to each other. For example, all the subspaces defined by $|\eta, i\rangle^0$ with $\eta \neq 0$ (i.e. excited vibronic states) are orthogonal to the subspace of the ground vibronic state. The sum total of all these subspaces with $\eta \neq 0$ (itself a subspace of total Hilbert space) is called the subspace complementary to the subspace of the ground vibronic state.

Besides these zeroth-order eigenfunctions, we shall also be interested in the eigenfunctions of the total Hamiltonian $\mathcal{H}$. In what follows, we shall assume that the effects of the perturbation $\lambda\mathcal{H}'$ are small enough that we can correlate the exact g_η eigenstates with their parent zero-order eigenstate η; thus we can usefully retain the quantum numbers η to define the exact eigenstates. (This is convenient but not essential). Thus after including the effects of the perturbation $\lambda\mathcal{H}'$, we have

$$\mathcal{H}|0, k\rangle = \left(E_0^0 + E_{0k}\right)|0, k\rangle, \tag{7.6}$$

$$\vdots$$

$$\mathcal{H}|\eta, k\rangle = \left(E_\eta^0 + E_{\eta k}\right)|\eta, k\rangle, \tag{7.7}$$

where the functions $|\eta, k\rangle$ are orthogonal and normalised to unity. Here we distinguish

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the g_η substates of a given η state by the quantum number k. There are, of course, g_η distinct values of k but we use it here rather than i to emphasise, as we shall see shortly, that there is not a one-to-one correspondence between the g_η exact eigenstates $|\eta, k\rangle$ and the g_η zeroth-order states $|\eta, i\rangle^0$ from which they arise. Since the sum total of the zeroth-order eigenfunctions $|\eta, i\rangle^0$ form a complete basis set (spanning total Hilbert space), we can expand each exact $|0, k\rangle$ eigenfunction in terms of this basis set:

$$|0, k\rangle = \sum_{\eta,i} c_{\eta i}^k |\eta, i\rangle^0. \tag{7.8}$$

The coefficients $c_{\eta i}^k$ can, in principle, be determined by solving the equations (7.6), (7.7), etc. Finally, we note that the states $|0, k\rangle$ may all be non-degenerate.

Now in microwave or radiofrequency spectroscopic investigations we are generally interested in groups of levels characterised by different values of one or two quantum numbers of the i type, but with the vibronic quantum number η remaining unchanged. For example, in rotational spectroscopy we measure primarily the energy dependence on rotational quantum number within a particular vibronic state, usually the ground state. It would be extremely inconvenient to have to work with the complete Hamiltonian $\mathcal{H}$ and to try to solve (7.6), (7.7), etc., completely; even with present day computers this would be a formidable task. Instead we seek to define an effective Hamiltonian $\mathcal{H}_{\text{eff}}(\eta)$ which contains the terms of primary interest, gives the correct eigenvalues $(E_\eta^0 + E_{\eta k})$, but which operates solely within the zeroth-order subspace of the vibronic state $|\eta\rangle^0$. The effects of terms off-diagonal in η will be contained in constants or parameters appearing in $\mathcal{H}_{\text{eff}}$. In our example, we are interested in deriving an effective Hamiltonian which operates solely within the i-dimensional subspace of the ground vibronic state. This effective Hamiltonian, $\mathcal{H}_{\text{eff}}(0)$, must therefore satisfy an eigenvalue equation of the form

$$\mathcal{H}_{\text{eff}}(0) \sum_i d_{0i}^k |0, i\rangle^0 = \left(E_0^0 + E_{0k}\right) \sum_i d_{0i}^k |0, i\rangle^0. \tag{7.9}$$

Each eigenfunction of $\mathcal{H}_{\text{eff}}(0)$ is some linear combination of the zeroth-order orthonormal set $|0, i\rangle^0$, as yet unspecified. Hence the problem we have to solve is to derive a general expression for $\mathcal{H}_{\text{eff}}(0)$ in terms of $\mathcal{H}^0$ and $\mathcal{H}'$.

Following Bloch [8], we shall tackle the problem through the use of certain projection operators, which we now define. The operator P_0 is defined by

$$P_0 = \sum_i |0, i\rangle^0 \ {}^0\langle 0, i|, \tag{7.10}$$

and projects any function onto the subspace spanned by the zeroth-order eigenfunctions with $\eta = 0$; for example,

$$\begin{aligned} P_0|0, k\rangle &= \sum_i |0, i\rangle^0 \ {}^0\langle 0, i \mid 0, k\rangle, \\ &= \sum_i |0, i\rangle^0 \ {}^0\langle 0, i| \sum_{\eta, j} c_{\eta j}^k |\eta, j\rangle^0, \\ &= \sum_i c_{0i}^k |0, i\rangle^0. \end{aligned} \tag{7.11}$$

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We note that the set of g_0 functions formed by projecting the eigenfunctions $|0, k\rangle$ onto the zeroth-order subspace of the ground vibronic state are, in general, neither orthogonal to each other nor normalised to unity. Also, as mentioned earlier, there is not necessarily a one-to-one correspondence between the quantum numbers k and i.

The operator Q_0 which is complementary to P_0 is given by

$$Q_0 = 1 - P_0 = \sum_i \sum_{\eta \neq 0} |\eta, i\rangle^0 \ {}^0\langle \eta, i|. \tag{7.12}$$

The effect of Q_0 on a particular function is to give the function's projection in the subspace complementary to the zeroth-order subspace of the ground vibronic state.

We also define the operator U, whose effect is essentially the opposite to that of P_0, i.e.

$$U \sum_i c_{0i}^k |0, i\rangle^0 = |0, k\rangle. \tag{7.13}$$

It is not difficult to show that the operator U must be given by

$$U = \sum_k \sum_j b_{0j}^k |0, k\rangle \ {}^0\langle 0, j|, \tag{7.14}$$

where the b coefficients are related to the c coefficients defined in (7.8) by the equation

$$\sum_i b_{0i}^k c_{0i}^{k'} = \delta_{kk'}. \tag{7.15}$$

We can readily prove the definition (7.14) of the operator U by expanding (7.13):

$$U \sum_i c_{0i}^k |0, i\rangle^0 = \sum_{j,k'} b_{0j}^{k'} |0, k'\rangle \ {}^0\langle 0, j| \sum_i c_{0i}^k |0, i\rangle^0 \tag{7.16}$$

$$= \sum_{j,k'} b_{0j}^{k'} |0, k'\rangle c_{0j}^k \tag{7.17}$$

$$= |0, k\rangle. \tag{7.18}$$

Equation (7.17) follows from the previous equation because of the orthogonality properties of the basis set, given by equation (7.4).

In our subsequent discussion we shall also require the results

$$UP_0 = U, \tag{7.19}$$

and

$$P_0 U = P_0. \tag{7.20}$$

Equation (7.19) follows readily from the definitions of P_0 and U. To verify (7.20) we consider the effect of the operator P_0U on an exact eigenfunction $|0, k\rangle$:

$$P_0 U|0, k\rangle = P_0 \sum_{i,k'} b_{0i}^{k'} |0, k'\rangle \ {}^0\langle 0, i \mid 0, k\rangle$$

$$= \sum_{i,j,k'} b_{0i}^{k'} c_{0j}^{k'} |0, j\rangle^0 \ {}^0\langle 0, i| \sum_{\eta,\ell} c_{\eta\ell}^k |\eta, \ell\rangle^0$$

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$$= \sum_{i,j,k'} b_{0i}^{k'} c_{0j}^{k'} c_{0i}^{k} |0, j\rangle^0$$
$$= \sum_{j} c_{0j}^{k} |0, j\rangle^0$$
$$= P_0 |0, k\rangle. \tag{7.21}$$

Consideration of the requirements of the effective Hamiltonian $\mathcal{H}_{\text{eff}}(0)$, equation (7.9), suggests that we might, with advantage, investigate the properties of the operator product $P_0 \lambda \mathcal{H}' U$, since U essentially projects the exact eigenfunctions $|0, k\rangle$ out of the zeroth-order subspace spanned by $|0, i\rangle^0$, $\lambda\mathcal{H}'$ operates on the exact eigenfunction according to (7.6) and (7.7), and P_0 projects back into the basis set within which we wish $\mathcal{H}_{\text{eff}}(0)$ to operate. Accordingly we operate with $\lambda P_0 \mathcal{H}' U$ on the zeroth-order basis functions with the following results:

$$\lambda P_0 \mathcal{H}' U \sum_i c_{0i}^{k} |0, i\rangle^0$$
$$= \lambda \sum_j |0, j\rangle^0 \, {}^0\langle 0, j|(\mathcal{H} - \mathcal{H}^0) U \sum_i c_{0i}^{k} |0, i\rangle^0 \tag{7.22}$$
$$= \lambda \sum_j |0, j\rangle^0 \left\{ {}^0\langle 0, j|\mathcal{H} U \sum_i c_{0i}^{k} |0, i\rangle^0 - {}^0\langle 0, j|\mathcal{H}^0 U \sum_i c_{0i}^{k} |0, i\rangle^0 \right\}$$
$$= \lambda \sum_j |0, j\rangle^0 \left\{ {}^0\langle 0, j|\mathcal{H}|0, k\rangle - {}^0\langle 0, j|\mathcal{H}^0 \sum_\ell b_{0\ell}^{k'} |0, k'\rangle \, {}^0\langle 0, \ell| \sum_i c_{0i}^{k} |0, i\rangle^0 \right\}$$
$$= \lambda \sum_j |0, j\rangle^0 \left\{ {}^0\langle 0, j \mid 0, k\rangle \left(E_0^0 + E_{0k}\right) - {}^0\langle 0, j|\mathcal{H}^0 \sum_\ell b_{0\ell}^{k'} |0, k\rangle c_{0\ell}^{k} \right\}$$
$$= \lambda \sum_j |0, j\rangle^0 \left\{ {}^0\langle 0, j| \sum_{\eta,\ell} c_{\eta\ell}^{k} |\eta, \ell\rangle^0 \left(E_0^0 + E_{0k}\right) - {}^0\langle 0, j|\mathcal{H}^0 \sum_{\eta,i} c_{\eta i}^{k} |\eta, i\rangle^0 \right\}$$
$$= \lambda \sum_j |0, j\rangle^0 \left\{ c_{0j}^{k} \left(E_0^0 + E_{0k}\right) - c_{0j}^{k} E_0^0 \right\}$$
$$= \lambda E_{0k} \sum_i c_{0i}^{k} |0, i\rangle^0. \tag{7.23}$$

We have now obtained the desired result because equation (7.23) is of the same form as (7.9) provided that we set $d_{0i}^{k} = c_{0i}^{k}$; in other words, the eigenfunctions of $P_0 \mathcal{H}' U$ are just the projections of the exact eigenfunctions $|0, k\rangle$ onto the zeroth-order subspace of the ground vibronic state. Comparison of equations (7.23) and (7.9) yields the relationship

$$\mathcal{H}_{\text{eff}}(0) = \mathcal{H}^0 + \lambda P_0 \mathcal{H}' U. \tag{7.24}$$

The final, but fairly lengthy, stage of this analysis is to seek a recurrence relation for U which allows us to express U in terms of P_0, Q_0 and $\mathcal{H}'$. First we note from (7.6)

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that

$$\left(\mathcal{H} - E_0^0\right)|0, k\rangle = E_{0k}|0, k\rangle. \tag{7.25}$$

Multiplying (7.25) on the left by P_0 yields

$$\lambda P_0 \mathcal{H}'|0, k\rangle = E_{0k} \sum_i c_{0i}^k |0, i\rangle^0. \tag{7.26}$$

The left-hand side of (7.26) follows because

$$P_0\left(\mathcal{H} - E_0^0\right) = P_0\left(\mathcal{H}^0 + \lambda\mathcal{H}' - E_0^0\right) = P_0\lambda\mathcal{H}'. \tag{7.27}$$

We now multiply (7.26) from the left by U to give

$$\lambda U P_0 \mathcal{H}'|0, k\rangle = E_{0k}|0, k\rangle. \tag{7.28}$$

Noting that $UP_0 = U$ (equation (7.19)) we rewrite (7.28) in the form

$$\lambda U\mathcal{H}'|0, k\rangle = E_{0k}|0, k\rangle, \tag{7.29}$$

$$= \left(\mathcal{H} - E_0^0\right)|0, k\rangle. \tag{7.30}$$

We therefore obtain the equation for the exact eigenfunctions $|0, k\rangle$,

$$\left(\mathcal{H} - E_0^0 - \lambda U\mathcal{H}'\right)|0, k\rangle = 0. \tag{7.31}$$

Multiplication on the right by $\sum_j b_{0j}^k\ {}^0\langle 0, j|$ and summation of the resultant expression over k gives:

$$\left(\mathcal{H} - E_0^0 - \lambda U\mathcal{H}'\right) \sum_{j,k} b_{0j}^k |0, k\rangle\ {}^0\langle 0, j| = \left(\mathcal{H} - E_0^0 - \lambda U\mathcal{H}'\right)U = 0. \tag{7.32}$$

Equation (7.32) can be rewritten as

$$\left(E_0^0 - \mathcal{H}^0\right)U = \lambda(\mathcal{H}'U - U\mathcal{H}'U) \tag{7.33}$$

Now since $Q_0 = 1 - P_0$, we can write

$$U = P_0U + Q_0U. \tag{7.34}$$

If we substitute this expression for U in the left-hand side of (7.33), and note that $(E_0^0 - \mathcal{H}^0)P_0$ is identically zero, we have

$$\left(E_0^0 - \mathcal{H}^0\right)Q_0U = \lambda(\mathcal{H}'U - U\mathcal{H}'U). \tag{7.35}$$

Now in the subspace complementary to that which is spanned by our zeroth-order basis set $|0, i\rangle^0$, the operator $(E_0^0 - \mathcal{H}^0)$ has a well defined inverse, which we denote by a^{-1}. Thus if we multiply (7.35) by Q_0a^{-1} we have

$$Q_0Q_0U = \lambda\frac{Q_0}{a}(\mathcal{H}'U - U\mathcal{H}'U), \tag{7.36}$$

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i.e.

$$Q_0 U = \lambda \frac{Q_0}{a}(\mathcal{H}' U - U\mathcal{H}' U). \tag{7.37}$$

Substituting (7.20) and (7.37) in (7.34), we finally obtain the recursion equation in U which we are seeking:

$$U = P_0 + \lambda \frac{Q_0}{a}(\mathcal{H}' U - U\mathcal{H}' U). \tag{7.38}$$

Now U can be expanded as a power series in the perturbation $\lambda\mathcal{H}'$; if we write U as a sum of zeroth-order, first-order, second-order, etc., contributions,

$$U = U^{(0)} + \lambda U^{(1)} + \lambda^2 U^{(2)} + \cdots, \tag{7.39}$$

we can then rewrite (7.38) in the form

$$\begin{aligned} &U^{(0)} + \lambda U^{(1)} + \lambda^2 U^{(2)} + \cdots \\ &\quad = P_0 + \lambda \frac{Q_0}{a}\{\mathcal{H}' U^{(0)} + \lambda \mathcal{H}' U^{(1)} + \lambda^2 \mathcal{H}' U^{(2)} + \cdots\} \\ &\qquad - \lambda \frac{Q_0}{a}\{U^{(0)}\mathcal{H}' U^{(0)} + \lambda U^{(1)}\mathcal{H}' U^{(0)} + \lambda^2 U^{(2)}\mathcal{H}' U^{(0)} + \cdots\} \\ &\qquad - \lambda \frac{Q_0}{a}\{\lambda U^{(0)}\mathcal{H}' U^{(1)} + \lambda^2 U^{(1)}\mathcal{H}' U^{(1)} + \lambda^3 U^{(2)}\mathcal{H}' U^{(1)} + \cdots\} \\ &\qquad - \lambda \frac{Q_0}{a}\{\lambda^2 U^{(0)}\mathcal{H}' U^{(2)} + \lambda^3 U^{(1)}\mathcal{H}' U^{(2)} + \lambda^4 U^{(2)}\mathcal{H}' U^{(2)} + \cdots\} + \cdots. \end{aligned} \tag{7.40}$$

Equating like powers of λ in equation (7.40) we obtain the results

$$\begin{aligned} U^{(0)} &= P_0, \\ U^{(1)} &= \frac{Q_0}{a}\{\mathcal{H}' U^{(0)} - U^{(0)}\mathcal{H}' U^{(0)}\}, \\ U^{(2)} &= \frac{Q_0}{a}\{\mathcal{H}' U^{(1)} - U^{(1)}\mathcal{H}' U^{(0)} - U^{(0)}\mathcal{H}' U^{(1)}\}, \\ &\cdots, \\ &\cdots, \\ U^{(n)} &= \frac{Q_0}{a}\left\{\mathcal{H}' U^{(n-1)} - \sum_{p=0}^{n-1} U^{(p)}\mathcal{H}' U^{(n-p-1)}\right\}. \end{aligned} \tag{7.41}$$

Noting that $U^{(0)} = P_0$ and that $(Q_0/a)P_0$ vanishes since Q_0 and P_0 are projection operators onto orthogonal subspaces, we see that we can remove the term $p = 0$ from the summation in the last line of (7.41). In other words, the general expression for $U^{(n)}$ is

$$U^{(n)} = \frac{Q_0}{a}\left\{\mathcal{H}' U^{(n-1)} - \sum_{p=1}^{n-1} U^{(p)}\mathcal{H}' U^{(n-p-1)}\right\}. \tag{7.42}$$

Using these results in equation (7.24) we are finally able to obtain an expression for

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the desired effective Hamiltonian, which is,

$$\begin{aligned}
\mathcal{H}_{\text{eff}}(0) &= \mathcal{H}^0 + \lambda P_0 \mathcal{H}' U \\
&= \mathcal{H}^0 + \lambda P_0 \mathcal{H}' U^{(0)} + \lambda^2 P_0 \mathcal{H}' U^{(1)} + \lambda^3 P_0 \mathcal{H}' U^{(2)} + \lambda^4 P_0 \mathcal{H}' U^{(3)} + \cdots \\
&= \mathcal{H}^0 + \lambda P_0 \mathcal{H}' P_0 + \lambda^2 P_0 \mathcal{H}' \frac{Q_0}{a} \mathcal{H}' P_0 \\
&\quad + \lambda^3 \left\{ P_0 \mathcal{H}' \frac{Q_0}{a} \mathcal{H}' \frac{Q_0}{a} \mathcal{H}' P_0 - P_0 \mathcal{H}' \frac{Q_0}{a^2} \mathcal{H}' P_0 \mathcal{H}' P_0 \right\} \\
&\quad + \lambda^4 \left\{ P_0 \mathcal{H}' \frac{Q_0}{a} \mathcal{H}' \frac{Q_0}{a} \mathcal{H}' \frac{Q_0}{a} \mathcal{H}' P_0 - P_0 \mathcal{H}' \frac{Q_0}{a} \mathcal{H}' \frac{Q_0}{a^2} \mathcal{H}' P_0 \mathcal{H}' P_0 \right. \\
&\quad - P_0 \mathcal{H}' \frac{Q_0}{a^2} \mathcal{H}' \frac{Q_0}{a} \mathcal{H}' P_0 \mathcal{H}' P_0 + P_0 \mathcal{H}' \frac{Q_0}{a^3} \mathcal{H}' P_0 \mathcal{H}' P_0 \mathcal{H}' P_0 \\
&\quad \left. - P_0 \mathcal{H}' \frac{Q_0}{a^2} \mathcal{H}' P_0 \mathcal{H}' \frac{Q_0}{a} \mathcal{H}' P_0 \right\} + \cdots . \qquad (7.43)
\end{aligned}$$

This expression is correct to fourth-order and higher-order terms can be obtained if required from the general expression for $U^{(n)}$. To remind the reader at this point, we recall that from equation (7.10),

$$P_0 = \sum_i |0, i\rangle^0 \ {}^0\langle 0, i|$$

and

$$(Q_0/a^r) = \sum_{\eta \neq 0} \sum_i |\eta, i\rangle^0 \ {}^0\langle \eta, i| / \left(E_0^0 - E_\eta^0\right)^r . \qquad (7.44)$$

We note that the operator $\mathcal{H}_{\text{eff}}(0)$ is constrained to act within the manifold of states $|0\rangle$ because each term on the right-hand side is sandwiched between a pair of projection operators, P_0.

The various contributions to the effective Hamiltonian operator on the right-hand side of equation (7.43) can be represented diagramatically in a way which is very helpful in practice. These diagrams are shown in figure 7.1. For each diagram, the position at the bottom refers to the chosen zeroth-order manifold $|0\rangle^0$ and the position at the top refers to the states in the complementary subspace. Each line joining these two positions stands for a connecting matrix element.

We shall return to the derivation of the individual terms of the effective Hamiltonian listed in (7.43) for some particular cases later in this chapter. To conclude this section, we now consider some of the general properties of the operator $\mathcal{H}_{\text{eff}}(0)$ and its eigenfunctions. Each of the terms listed in (7.43) is composed of products of the three operators P_0, Q_0 and $\mathcal{H}'$. Although each of these operators is individually Hermitian (i.e. the operator is self-adjoint, $\mathrm{P}_0^\dagger = \mathrm{P}_0$), a product of any of them is not necessarily Hermitian. In fact, a term is only Hermitian when it is palindromic, that is, when it reads the same forwards as backwards. Inspection of equation (7.43) reveals that $\mathcal{H}_{\text{eff}}(0)$ is Hermitian up to and including terms in λ^2 but that there are non-Hermitian terms in the λ^3 and higher-order contributions. The nature of these non-Hermitian properties can

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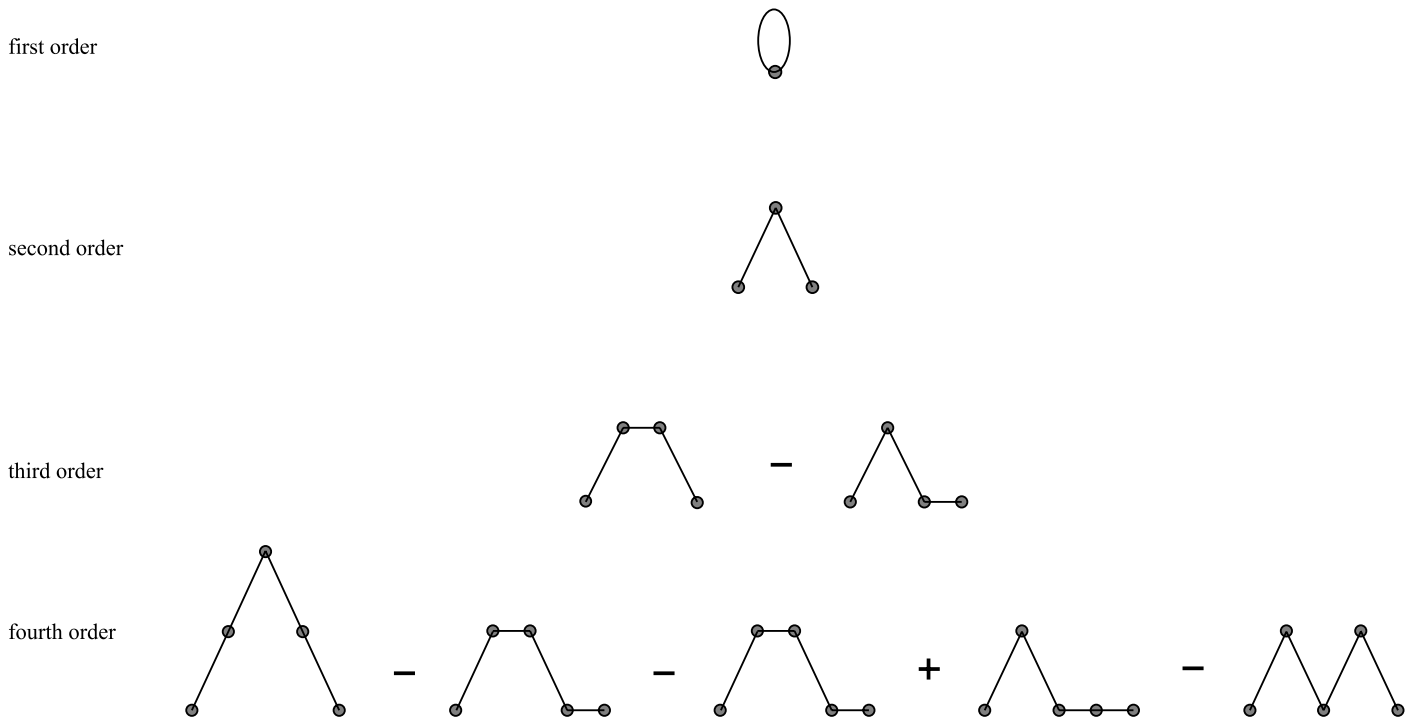

Figure 7.1. Diagrammatic representation of the various contributions to the effective Hamiltonian given in equation (7.43) (see text).

be understood by referring back to eigenvalue equations for $\mathcal{H}_{\text{eff}}(0)$, equations (7.9) and (7.23). Because we have constructed $\mathcal{H}_{\text{eff}}(0)$ to have eigenvalues identical with those of the total Hamiltonian $\mathcal{H}$ (which is, of course, Hermitian), $\mathcal{H}_{\text{eff}}(0)$ will have real eigenvalues, even though it is non-Hermitian. However, we recall that the eigenfunctions of $\mathcal{H}_{\text{eff}}(0)$ are $\sum_i c_{0i}^k |0, i\rangle^0$, the projections of the actual eigenfunctions of $\mathcal{H}$ onto a zeroth-order subspace. These eigenfunctions are not necessarily orthogonal or normalised with respect to each other and it is in this way that the non-Hermitian properties of the operator $\mathcal{H}_{\text{eff}}(0)$ manifest themselves.

Since we shall usually be more interested in the eigenvalues than the eigenfunctions of $\mathcal{H}_{\text{eff}}(0)$, the possible non-Hermitian properties need not concern us too deeply. However, there may be certain situations, for example in the use of computer programmes to extract the eigenvalues of $\mathcal{H}_{\text{eff}}(0)$, where we must take account of the non-orthogonal eigenfunctions. In these situations, it is easiest to use a symmetrised form of the non-Hermitian terms in $\mathcal{H}_{\text{eff}}(0)$; in the third order, this would be

$$-\frac{1}{2}\lambda^3 \left\{ P_0 \mathcal{H}' \frac{Q_0}{a^2} \mathcal{H}' P_0 \mathcal{H}' P_0 + P_0 \mathcal{H}' P_0 \mathcal{H}' \frac{Q_0}{a^2} \mathcal{H}' P_0 \right\}. \tag{7.45}$$

Soliverez [9] has shown that errors introduced by this modification of equation (7.43) only appear in fifth and higher orders. Since in practice it is rarely worthwhile to use perturbation theory beyond third order, these discrepancies need not worry us.

7.3. The Van Vleck and contact transformations

We now describe two other methods of deriving an effective Hamiltonian, both of which are widely used. Although we shall not go into details, the mathematical development will show that the two methods are exactly equivalent and, in addition, that they are very nearly equivalent to the method based on projection operators given in the previous section. The equivalence of the three methods is not really very surprising since they are all solutions of the problem by perturbation theory, differing only in the mathematical techniques employed.

Again we start by partitioning the total Hamiltonian,

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}', \tag{7.46}$$

where all terms off-diagonal in the quantum number η are included in $\mathcal{H}'$. We note that since we choose our zeroth-order Hamiltonian to be independent of operators involving the quantum numbers i (see previous section), our zeroth-order eigenfunctions $|\eta, i\rangle^0$ can be completely factorised into the product

$$|\eta, i\rangle^0 = |\eta\rangle^0 |i\rangle^0, \tag{7.47}$$

where $|\eta\rangle^0$ are the eigenfunctions of $\mathcal{H}^0$,

$$\mathcal{H}^0 |\eta\rangle^0 = E_n^0 |\eta\rangle^0. \tag{7.48}$$

We first imagine that we have constructed a matrix representation of $\mathcal{H}$ in the

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zeroth-order basis set (7.47), and we then subject this matrix to a similarity transformation to give a transformed matrix $\tilde{\mathcal{H}}$ where

$$\tilde{\mathcal{H}} = T^{-1}\mathcal{H}T. \tag{7.49}$$

Since the matrix T is unitary ($T^{\dagger} = T^{-1}$), $\tilde{\mathcal{H}}$ will have the same eigenvalues as $\mathcal{H}$ but different eigenfunctions. We then set

$$T = \mathrm{e}^{\mathrm{i}\lambda S_1}\mathrm{e}^{\mathrm{i}\lambda^2 S_2}\mathrm{e}^{\mathrm{i}\lambda^3 S_3}\ldots, \tag{7.50}$$

where S_n is Hermitian and S_1, S_2, S_3, ..., are chosen in the way outlined below to remove the effects of matrix elements off-diagonal in η to order λ, λ^2, λ^3, ... Each of the successive transformations produced by the development of T (7.50) is known as a *contact transformation* [10, 11], while the first ($\mathrm{e}^{-\mathrm{i}\lambda S_1}\mathcal{H}\mathrm{e}^{\mathrm{i}\lambda S_1}$) is what is usually referred to as the *Van Vleck transformation* [12, 13].

We now expand $\tilde{\mathcal{H}}$ as

$$\tilde{\mathcal{H}} = \tilde{\mathcal{H}}_0 + \lambda\tilde{\mathcal{H}}_1 + \lambda^2\mathcal{H}_2 + \ldots, \tag{7.51}$$

and equate the right-hand side with

$$\ldots \mathrm{e}^{-\mathrm{i}\lambda^2 S_2}\mathrm{e}^{-\mathrm{i}\lambda S_1}(\mathcal{H}^0 + \lambda\mathcal{H}')\mathrm{e}^{\mathrm{i}\lambda S_1}\mathrm{e}^{\mathrm{i}\lambda^2 S_2}\ldots. \tag{7.52}$$

Comparing coefficients of λ, we can obtain the results

$$\lambda^0: \quad \tilde{\mathcal{H}}_0 = \mathcal{H}^0. \tag{7.53}$$

$$\lambda^1: \quad \tilde{\mathcal{H}}_1 = \mathcal{H}' + \mathrm{i}[\mathcal{H}^0, S_1]. \tag{7.54}$$

$$\lambda^2: \quad \tilde{\mathcal{H}}_2 = \mathrm{i}[\mathcal{H}^0, S_2] + \mathrm{i}[\mathcal{H}', S_1] + \frac{1}{2}[[S_1, \mathcal{H}^0], S_1]. \tag{7.55}$$

$$\lambda^3: \quad \tilde{\mathcal{H}}_3 = \mathrm{i}[\mathcal{H}^0, S_3] + \mathrm{i}[\mathcal{H}', S_2] - \frac{\mathrm{i}}{6}[[[\mathcal{H}^0, S_1], S_1], S_1] + \frac{1}{2}[[S_1, \mathcal{H}'], S_1] + [S_2, [\mathcal{H}^0, S_1]]. \tag{7.56}$$

Substituting (7.54) into (7.55) and (7.56), we have

$$\tilde{\mathcal{H}}_2 = \mathrm{i}[\mathcal{H}^0, S_2] + \frac{\mathrm{i}}{2}[\mathcal{H}', S_1] + \frac{\mathrm{i}}{2}[\tilde{\mathcal{H}}_1, S_1]. \tag{7.57}$$

$$\tilde{\mathcal{H}}_3 = \mathrm{i}[\mathcal{H}^0, S_3] + \mathrm{i}[\tilde{\mathcal{H}}_1, S_2] - \frac{1}{3}[[\mathcal{H}', S_1], S_1] - \frac{1}{6}[[\tilde{\mathcal{H}}_1, S_1], S_1]. \tag{7.58}$$

We now show how the matrix elements of S_1 can be selected to remove the effects on $\mathcal{H}$ of matrix elements off-diagonal in η. Since it can easily be verified that ${}^0\langle\eta, i|[\mathcal{H}^0, S_1]|\eta, j\rangle^0$ is always zero, irrespective of the form of S_1, we see from (7.54) that the diagonal matrix elements of $\tilde{\mathcal{H}}_1$ are just the diagonal matrix elements of $\mathcal{H}'$:

$${}^0\langle\eta, i|\tilde{\mathcal{H}}_1|\eta, j\rangle^0 = {}^0\langle\eta, i|\mathcal{H}'|\eta, j\rangle^0. \tag{7.59}$$

Without any loss in generality therefore, we can set the matrix elements of S_1 diagonal

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in η equal to zero:

$$ {}^0\langle \eta, i|S_1|\eta, j\rangle^0 = 0 \quad \text{for all } \eta. \tag{7.60} $$

In addition, we require the matrix elements of $\tilde{\mathcal{H}}_1$ off-diagonal in η to be zero, that is, from (7.54):

$$ {}^0\langle \eta, i|\tilde{\mathcal{H}}_1|\eta', j\rangle^0 = {}^0\langle \eta, i|\mathcal{H}'|\eta', j\rangle^0 + \mathrm{i}\ {}^0\langle \eta, i|S_1|\eta', j\rangle^0\left(E^0_\eta - E^0_{\eta'}\right) = 0 \quad \text{for } \eta' \neq \eta. \tag{7.61} $$

Thus

$$ \mathrm{i}\ {}^0\langle \eta, i|S_1|\eta', j\rangle^0 = -\frac{{}^0\langle \eta, i|\mathcal{H}'|\eta', j\rangle^0}{\left(E^0_\eta - E^0_{\eta'}\right)}. \tag{7.62} $$

The matrix elements of S_2 are chosen in a similar fashion so that ${}^0\langle \eta, i|\tilde{\mathcal{H}}_2|\eta', j\rangle^0$ is zero, and so on.

We now consider the diagonal matrix elements of $\tilde{\mathcal{H}}_2$ and $\tilde{\mathcal{H}}_3$ using the results (7.60) and (7.62). It is a simple matter to establish that for $\tilde{\mathcal{H}}_2$, equation (7.57), only the second term on the right-hand side has non-zero diagonal matrix elements,

$$ {}^0\langle \eta, i|\tilde{\mathcal{H}}_2|\eta, j\rangle^0 = \frac{\mathrm{i}}{2}\ {}^0\langle \eta, i|[\mathcal{H}', S_1]|\eta, i\rangle^0, \tag{7.63} $$

while for $\tilde{\mathcal{H}}_3$, equation (7.58), only the third and fourth terms have non-zero diagonal matrix elements, irrespective of the forms of S_2 and S_3:

$$ {}^0\langle \eta, i|\tilde{\mathcal{H}}_3|\eta, j\rangle^0 = -\frac{1}{3}\ {}^0\langle \eta, i|[[\mathcal{H}', S_1], S_1]|\eta, j\rangle^0 - \frac{1}{6}\ {}^0\langle \eta, i|[[\tilde{\mathcal{H}}_1, S_1], S_1]|\eta, j\rangle^0. \tag{7.64} $$

Thus if we are only interested in deriving an effective Hamiltonian up to order λ^3, we need not concern ourselves with the explicit forms of S_2 and S_3. Furthermore, for the particular situation where $\mathcal{H}'$ only has matrix elements which are off-diagonal in η (i.e. all diagonal matrix elements of $\mathcal{H}'$ are zero), the second term in (7.64) also vanishes and we have

$$ {}^0\langle \eta, i|\tilde{\mathcal{H}}_3|\eta, j\rangle^0 = -\frac{1}{3}\ {}^0\langle \eta, i|[[\mathcal{H}', S_1], S_1]|\eta, j\rangle^0. \tag{7.65} $$

Thus for the general case, we can separate the matrix elements of $\mathcal{H}'$ into diagonal and off-diagonal categories and use (7.65) to evaluate contributions to $\tilde{\mathcal{H}}_3$ involving off-diagonal matrix elements of $\mathcal{H}'$ and to use, from (7.59) and (7.64),

$$ {}^0\langle \eta, i|\tilde{\mathcal{H}}_3|\eta, j\rangle^0 = -\frac{1}{2}\ {}^0\langle \eta, i|[[\mathcal{H}', S_1], S_1]|\eta, j\rangle^0, \tag{7.66} $$

for contributions from diagonal elements.

In vibration–rotation theory, the λ, λ^2 and λ^3 contributions to the contact-transformed Hamiltonian are commonly evaluated directly from the relationships (7.59), (7.63), (7.65) and (7.66). This is because the particularly simple commutation relationships which exist between the normal coordinate operator Q, its conjugate

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momentum P and the simple harmonic oscillator Hamiltonian, which is commonly taken as $\mathcal{H}^0$ in equation (7.46), make the evaluation of the commutator brackets quite straightforward. However, equations (7.59), (7.63), (7.65) and (7.66) are not very suitable for the derivation of an effective Hamiltonian that includes the effects of matrix elements of $\mathcal{H}'$ off-diagonal in electronic state, since the commutation relations between $\mathcal{H}^0$ and the operators involved are generally much more complicated. In this situation, it is easier to develop the various contributions in terms of matrix element products using equation (7.62). After some straightforward algebra, we obtain the alternative but completely equivalent results,

$$ {}^0\langle \eta, i|\tilde{\mathcal{H}}_0|\eta, j\rangle^0 = E^0_\eta. \tag{7.67} $$

$$ {}^0\langle \eta, i|\tilde{\mathcal{H}}_1|\eta, j\rangle^0 = {}^0\langle \eta, i|\mathcal{H}'|\eta, j\rangle^0. \tag{7.68} $$

$$ {}^0\langle \eta, i|\tilde{\mathcal{H}}_2|\eta, j\rangle^0 = \sum_{\eta'\neq\eta}\sum_k \frac{{}^0\langle \eta, i|\mathcal{H}'|\eta', k\rangle^0\ {}^0\langle \eta', k|\mathcal{H}'|\eta, j\rangle^0}{\left(E^0_\eta - E^0_{\eta'}\right)}. \tag{7.69} $$

$$ \begin{aligned} {}^0\langle \eta, i|\tilde{\mathcal{H}}_3|\eta, j\rangle^0 = {} & \sum_{\eta',\eta''\neq\eta}\sum_{k,\ell} \frac{{}^0\langle \eta, i|\mathcal{H}'|\eta', k\rangle^0\ {}^0\langle \eta', k|\mathcal{H}'|\eta'', \ell\rangle^0\ {}^0\langle \eta'', \ell|\mathcal{H}'|\eta, j\rangle^0}{\left(E^0_\eta - E^0_{\eta'}\right)\left(E^0_\eta - E^0_{\eta''}\right)} \\ & - \frac{1}{2}\sum_{\eta'\neq\eta}\sum_{k,\ell}\left\{ \frac{{}^0\langle \eta, i|\mathcal{H}'|\eta, k\rangle^0\ {}^0\langle \eta, k|\mathcal{H}'|\eta', \ell\rangle^0\ {}^0\langle \eta', \ell|\mathcal{H}'|\eta, j\rangle^0}{\left(E^0_\eta - E^0_{\eta'}\right)^2} \right. \\ & \left. + \frac{{}^0\langle \eta, i|\mathcal{H}'|\eta', k\rangle^0\ {}^0\langle \eta', k|\mathcal{H}'|\eta, \ell\rangle^0\ {}^0\langle \eta, \ell|\mathcal{H}'|\eta, j\rangle^0}{\left(E^0_\eta - E^0_{\eta'}\right)^2} \right\}. \end{aligned} \tag{7.70} $$

If we compare these equations with the projection operator expansion given in equation (7.43), we find that the expressions are identical up to and including the λ^2 contribution but that the λ^3 term derived here corresponds not to the λ^3 term in the expansion (7.43) but to its symmetrised (Hermitian) form discussed at the end of section 7.2. Since the discrepancies that arise from these two different forms are of order λ^5 or higher, the effective Hamiltonians derived by the two methods are identical to order λ^3. In the literature the Van Vleck transformation is normally implemented by use of equations (7.67) to (7.70) although the λ^3 contribution (7.70) has often been ignored.

In conclusion, we note that thus far we have derived matrix elements of the transformed Hamiltonian $\tilde{\mathcal{H}}$ for a given block in the complete matrix labelled by a particular value of η rather than an effective Hamiltonian operating only within the subspace of the state η. It is an easy matter to cast our results in the form of an effective Hamiltonian for any particular case since the matrix elements involved in either the commutator bracket formulation (contact transformation) or the explicit matrix element formulation (Van Vleck transformation) can always be factorised into a product of a matrix element of operators involved in $\mathcal{H}^0$ associated with the quantum number η and a matrix element of operators that act only within the subspace levels of a given η state, associated with the quantum number i. This follows because the basis set can be factorised as in equation (7.47). The matrix element involving the η quantum number can then either be evaluated or included as a parameter to be determined experimentally, while the

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matrix element involving the i quantum number can be restored to operator form with the restriction that it only operates on the functions $|i\rangle^0$ which span a particular state $|\eta\rangle^0$. We shall see later in this chapter how this process is carried out in detail.

7.4. Effective Hamiltonian for a diatomic molecule in a given electronic state

7.4.1. Introduction

It is well known from the Born–Oppenheimer separation [1] that the pattern of energy levels for a typical diatomic molecule consists first of widely separated electronic states ($\Delta E_{\text{elec}} \approx 20\,000$ cm^{-1}) . Each of these states then supports a set of more closely spaced vibrational levels ($\Delta E_{\text{vib}} \approx 1000$ cm^{-1}). Each of these vibrational levels in turn is spanned by closely spaced rotational levels ($\Delta E_{\text{rot}} \approx 1$ cm^{-1}) and, in the case of open shell molecules, by fine and hyperfine states ($\Delta E_{\text{fs}} \approx 100$ cm^{-1} and $\Delta E_{\text{hfs}} \approx 0.01$ cm^{-1}). The objective is to construct an effective Hamiltonian which is capable of describing the detailed energy levels of the molecule in a single vibrational level of a particular electronic state. It is usual to derive this Hamiltonian in two stages because of the different nature of the electronic and nuclear coordinates. In the first step, which we describe in the present section, we derive a Hamiltonian which acts on all the vibrational states of a single electronic state. The operators thus remain explicitly dependent on the vibrational coordinate R (the internuclear separation). In the second step, described in section 7.55, we remove the effects of terms in this intermediate Hamiltonian which couple different vibrational levels. The result is an effective Hamiltonian for each vibronic state.

In this section, we shall use the degenerate perturbation theory approach to derive the form of the effective Hamiltonian for a diatomic molecule in a given electronic state. Exactly the same result can be obtained by use of the Van Vleck or contact transformations [12, 13]. The general expression for the operator up to fourth order in perturbation theory is given in equation (7.43). Fourth order can be considered as the practical limit to this type of approach. Indeed, even its implementation is very laborious and has only been used to investigate the form of certain special terms in the effective Hamiltonian. We shall consider some of these terms later in this chapter. For the moment we confine our attention to first- and second-order effects only.

To simplify matters, we shall start out by considering the effective Hamiltonian for a molecule in the absence of external fields. The additional effects of magnetic or electric fields will be dealt with later. We have derived the fundamental Hamiltonian for a diatomic molecule in chapters 2 to 4. For the present purposes it can be written:

$$\mathcal{H} = \mathcal{H}_{\text{elec}} + \frac{1}{2\mu}\boldsymbol{P}_R^2 + hcB(R)(\boldsymbol{N}-\boldsymbol{L})^2 + \frac{1}{2M}\boldsymbol{P}^2 + \mathcal{H}_{\text{so}}^{(\text{e})} + \mathcal{H}_{\text{so}}^{(\text{n})} + \mathcal{H}_{\text{ss}}^{(\text{scal})} + \mathcal{H}_{\text{ss}}^{(\text{tens})} + \mathcal{H}_{\text{hfs}}. \tag{7.71}$$

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The first term consists of both the kinetic energy of the electrons and the complete Coulomb energy, the second is the vibrational kinetic energy, the third is the rotational kinetic energy, the fourth is the 'mass polarisation' energy involving the total linear momentum of the electrons $\boldsymbol{P} = \sum_i \boldsymbol{p}_i$, the fifth and sixth are the parts of the electronic spin–orbit and spin–other-orbit operators which contain the electronic and nuclear momenta respectively, the seventh and eight terms are the scalar and tensor parts of the electron spin–spin interaction, and the last term describes the nuclear hyperfine effects (both magnetic and electric). In equation (7.71), μ and M are the reduced and total masses of the nuclei respectively, the rotational variable $B(R)$ is $\hbar^2/2hc\mu R^2$ (in cm^{-1}), and $\hbar\boldsymbol{L}$ is the electron orbital angular momentum about the nuclear centre of mass. $\boldsymbol{N}$ is equal to $\boldsymbol{J} - \boldsymbol{S}$, where $\hbar\boldsymbol{J}$ is the total angular momentum apart from nuclear spin, and $\hbar\boldsymbol{S}$ is the electron spin angular momentum; as elsewhere in this book, the angular momenta are dimensionless.

The explicit forms of terms five to eight in equation (7.71) are as follows:

$$\mathcal{H}_{\mathrm{so}}^{(\mathrm{e})} = \frac{\hbar e^2 g_S}{16\pi\varepsilon_0 m_e^2 c^2} \sum_i \boldsymbol{s_i} \cdot \left\{ \sum_\alpha Z_\alpha r_{i\alpha}^{-3} (\boldsymbol{r}_i - \boldsymbol{r}_\alpha) \wedge \boldsymbol{p}_i - \sum_{j \neq i} r_{ij}^{-3} (\boldsymbol{r}_i - \boldsymbol{r}_j) \wedge (\boldsymbol{p}_i - 2\boldsymbol{p}_j) \right\}. \tag{7.72}$$

$$\mathcal{H}_{\mathrm{so}}^{(n)} = -\frac{\hbar e^2 g_S}{8\pi\varepsilon_0 m_e c^2} \sum_i \boldsymbol{s_i} \cdot \left\{ \sum_\alpha Z_\alpha M_\alpha^{-1} r_{i\alpha}^{-3} (\boldsymbol{r}_i - \boldsymbol{r}_\alpha) \wedge \boldsymbol{P}_\alpha \right\}. \tag{7.73}$$

$$\mathcal{H}_{\mathrm{ss}}^{(\mathrm{scal})} = -\frac{\hbar^2 e^2 g_S^2}{6\varepsilon_0 m_e^2 c^2} \sum_i \sum_{j>i} (\boldsymbol{s}_i \cdot \boldsymbol{s}_j) \delta(\boldsymbol{r}_{ij}). \tag{7.74}$$

$$\mathcal{H}_{\mathrm{ss}}^{(\mathrm{tens})} = \frac{\hbar^2 e^2 g_S^2}{16\pi\varepsilon_0 m_e^2 c^2} \sum_i \sum_{j>i} \left[\boldsymbol{s}_i \cdot \boldsymbol{s}_j - 3(\boldsymbol{s}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{s}_j \cdot \boldsymbol{r}_{ij}) r_{ij}^{-2} \right] \left[r_{ij}^{-3} - (4\pi/3)\delta(\boldsymbol{r}_{ij}) \right]. \tag{7.75}$$

The subscripts i, j refer to electrons, α refers to nuclei, and ε_0 is the permittivity of free space. These terms were listed at the end of chapter 3, where their derivation was described.

We now proceed to remove the effects of the terms in equation (7.71) which couple different electronic states. For a molecule in which the spin–orbit coupling matrix elements are small compared with the electronic intervals, a convenient starting point is the set of Hund's case (a) electronic state vectors $|\eta, \Lambda, (S), \Sigma; R\rangle$ which are obtained by solving the electronic Schrödinger equation,

$$\mathcal{H}_{\mathrm{elec}} |\eta, \Lambda, (S), \Sigma; R\rangle = |\eta, \Lambda, (S), \Sigma; R\rangle V_\eta(R), \tag{7.76}$$

as a function of the internuclear separation R. Here η is a state symbol (such as $X^2\Pi$) specifying the electronic state in question, which has two-fold degenerate orbital components $\Lambda = \pm|\Lambda|$ if $\Lambda \neq 0$. Although $\mathcal{H}_{\mathrm{elec}}$ is a purely orbital operator, the electronic permutation symmetry of the orbital eigenvectors determines the electron spin quantum number S through the Pauli principle [14]. The $(2S+1)$ different Σ components of S are degenerate with each other at the level of approximation defined by equation (7.76).

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The notation for the state vector in this equation is redundant since S is contained in η but it is useful to emphasise that S has a definite value (unlike L for a diatomic molecule).

We shall use equation (7.76) as the basis for a perturbation treatment of the full Hamiltonian $\mathcal{H}$. Thus $\mathcal{H}_{\rm elec}$ is the zeroth-order Hamiltonian, see equation (7.1). Consequently the kets $|\eta, \Lambda, (S), \Sigma; R\rangle$ are the zeroth-order eigenstates and $V_\eta(R)$ are the zeroth-order eigenvalues, see equation (7.2). The perturbation process has the effect of removing terms which give matrix elements off-diagonal in η without altering the eigenvalues of $\mathcal{H}$ (at least, to a desired level of accuracy). In performing these calculations, one should remember that the electronic matrix elements of $\mathcal{H}$ are operators in the space of the vibrational, rotational and spin degrees of freedom. From equation (7.43), we can write the matrix elements of the transformed Hamiltonian $\mathcal{H}'$ to the second order as follows:

$$\begin{aligned}
&\langle \eta, \Lambda, (S), \Sigma; R|\mathcal{H}'|\eta', \Lambda', (S'), \Sigma'; R\rangle \\
&\quad = \delta_{\eta\eta'}\delta_{SS'} \Bigg\{ \langle \eta, \Lambda, (S), \Sigma; R|\mathcal{H}|\eta, \Lambda', (S), \Sigma'; R\rangle \\
&\qquad + \sum_{\eta''\neq\eta, \Lambda'', \Sigma''} \langle \eta, \Lambda, (S), \Sigma; R|\mathcal{H}|\eta'', \Lambda'', (S''), \Sigma''; R\rangle \\
&\qquad \times \langle \eta'', \Lambda'', (S''), \Sigma''; R|\mathcal{H}|\eta, \Lambda', (S), \Sigma'; R\rangle / [V_\eta(R) - V_{\eta''}(R)] \Bigg\}. \quad (7.77)
\end{aligned}$$

The condition for the validity of this approach to the perturbation treatment is

$$|\langle \eta, \Lambda, (S), \Sigma; R|\mathcal{H}|\eta'', \Lambda'', (S), \Sigma''; R\rangle| \ll |V_\eta(R) - V_{\eta''}(R)| \quad (7.78)$$

for all Λ, Σ, Λ'', Σ'' with $\eta \neq \eta''$. If this relationship is not satisfied, a different zeroth-order coupling case must be adopted. Instead of working in terms of matrix elements, it is usually more illuminating to employ an effective Hamiltonian operator $\mathcal{H}_\eta$ for the electronic state η. This is an operator in the space of the Λ and Σ components of η as well as the space of the vibrational and rotational degrees of freedom and is an equivalent operator defined so that its matrix elements are equal to those of $\mathcal{H}'$:

$$\langle \Lambda, S, \Sigma|\mathcal{H}_\eta|\Lambda', S, \Sigma'\rangle = \langle \eta, \Lambda, (S), \Sigma; R|\mathcal{H}'|\eta, \Lambda', (S), \Sigma'; R\rangle. \quad (7.79)$$

Thus, what we call $\mathcal{H}_\eta$ here is the same as the operator $\mathcal{H}_{\rm eff}(0)$ in equation (7.43) which acts only within the manifold of states $|0\rangle$.

In the present treatment, we retain essentially all the diagonal matrix elements of $\mathcal{H}$; these are the first-order contributions to the effective electronic Hamiltonian. There are many possible off-diagonal matrix elements but we shall consider only those due to the terms in $\mathcal{H}_{\rm rot}$ and $\mathcal{H}^{\rm e}_{\rm so}$ here since these are the largest and provide readily observable effects. The appropriate part of the rotational Hamiltonian is $-2hcB(R)(N_xL_x + N_yL_y)$. The matrix elements of this operator are comparatively sparse because they are subject to the selection rules $\Delta\Lambda = \pm 1$, $\Delta S = 0$ and $\Delta\Sigma = 0$. The spin–orbit coupling term, on the other hand, has a much more extensive set of matrix elements allowed

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by the selection rules $\Delta\Omega = 0$, $\Delta S = 0, \pm 1$ and $\Delta\Sigma = -\Delta\Lambda = 0, \mp 1$. In order to see how the effective Hamiltonian is derived, we now deal with some of the contributions explicitly.

7.4.2. The rotational Hamiltonian

The simplest example of the way in which the various terms arise in the effective electronic Hamiltonian involves the rotational kinetic energy operator, $\mathcal{H}_{\rm rot}$:

$$\begin{aligned} \mathcal{H}_{\rm rot} &= hcB(R)\boldsymbol{R}^2 \\ &= hcB(R)(\boldsymbol{N}-\boldsymbol{L})^2, \end{aligned} \tag{7.80}$$

where $\hbar\boldsymbol{R}$ is the end-over-end rotational angular momentum of the nuclei, and

$$B(R) = \hbar^2/(2\mu R^2 hc). \tag{7.81}$$

The operators $B(R)$ and $\boldsymbol{N}$ act only within each electronic state while the orbital angular momentum $\boldsymbol{L}$ acts both within and between such states.

The first-order contribution to the effective Hamiltonian involves the diagonal matrix element of the operator in equation (7.80):

$$\begin{aligned} \mathcal{H}_{\rm eff}^{(1)}/hc &= |0\rangle\langle 0|B(R)(\boldsymbol{N}-\boldsymbol{L})^2|0\rangle\langle 0| \\ &= B^{(1)}(R)\big(\boldsymbol{N}^2 - L_z^2\big), \end{aligned} \tag{7.82}$$

where

$$B^{(1)}(R) = \langle 0, \Lambda|B(R)|0, \Lambda\rangle, \tag{7.83}$$

because the z component of $(\boldsymbol{N}-\boldsymbol{L})$, which is the only component of $\boldsymbol{L}$ which gives a diagonal matrix element, vanishes. Note that when we use the term *diagonal* in this context, we mean diagonal within the zeroth-order states of $|0\rangle$. The second-order contribution arises from the admixture of other electronic states $|\eta\rangle$ into the state in question $|0\rangle$ through the operator components L_x and L_y in the form $-hcB(R)(N_+L_- + N_-L_+)$:

$$\begin{aligned} &\mathcal{H}_{\rm eff}^{(2)}/hc \\ &= hc|0\rangle \sum_{\eta\neq 0} \frac{\langle 0|-B(R)(N_+L_- + N_-L_+)|\eta\rangle\langle\eta|-B(R)(N_+L_- + N_-L_+)|0\rangle\langle 0|}{[V_0(R) - V_\eta(R)]} \\ &= hc \sum_{\eta\neq 0,\,\Lambda'} \frac{\langle 0, \Lambda|B(R)L_\mp|\eta, \Lambda'\rangle\langle\eta, \Lambda'|B(R)L_\pm|0, \Lambda\rangle}{[V_0(R) - V_\eta(R)]}(N_\pm N_\mp) \\ &= B^{(2)}(R)\big(N_x^2 + N_y^2\big) \\ &= B^{(2)}(R)\big(\boldsymbol{N}^2 - N_z^2\big). \end{aligned} \tag{7.84}$$

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The second-order contribution to $B(R)$ is thus given by

$$B^{(2)}(R) = hc \sum_{\eta \neq 0} \frac{\langle 0, \Lambda | B(R) L_{\mp} | \eta, \Lambda' \rangle \langle \eta, \Lambda' | B(R) L_{\pm} | 0, \Lambda \rangle}{[V_0(R) - V_\eta(R)]}. \tag{7.85}$$

Hence, to second order, we can write the effective rotational Hamiltonian as

$$\mathcal{H}_{\text{rot}} = B(R)\big(\boldsymbol{N}^2 - N_z^2\big), \tag{7.86}$$

where

$$B(R) = B^{(1)}(R) + B^{(2)}(R). \tag{7.87}$$

Since the matrix element of N_z^2 is constant for a given electronic state ($= \Lambda^2$), we see from equation (7.87) that the second-order contribution has exactly the same operator form as the first-order contribution. The effects of the matrix elements off-diagonal in electronic state are therefore absorbed in the Hamiltonian to give an operator of exactly the same form as in the full Hamiltonian, but with a slightly modified coefficient $B(R)$. Physically, the first-order contribution $B^{(1)}(R)$ describes the rotational kinetic energy from the motion of the bare nuclei and the second-order contribution $B^{(2)}(R)$ adds in the contribution to the kinetic energy from the electrons which rotate in laboratory space with the nuclei. (The electrons follow the motion of the nuclei very closely because of the Coulombic attraction between them.) We see also from its definition in (7.81) that the first-order contribution to $B(R)$ is proportional to μ^{-1} whereas $B^{(2)}(R)$ is proportional to μ^{-2}, provided that $[V_0(R) - V_\eta(R)]$ is large compared with the off-diagonal matrix elements. The ratio of the two contributions will therefore vary between different isotopic forms of the molecule and can thus, in principle, be separated. This difference in reduced mass dependence must be taken into account when modelling the effects of isotopic substitution on rotational energy levels.

We see from the way in which the effective rotational Hamiltonian is constructed that it is naturally expressed in terms of the angular momentum operator $\boldsymbol{N}$. In the scientific literature, however, it is frequently written in terms of the vector $\boldsymbol{R}$ (which represents the rotational angular momentum of the nuclei) rather than $\boldsymbol{N}$. While $\boldsymbol{R} = \boldsymbol{N} - \boldsymbol{L}$ occurs in the fundamental Hamiltonian (7.71), its use in the effective Hamiltonian is not satisfactory because $\boldsymbol{R}$ has matrix elements (due to $\boldsymbol{L}$) which connect different electronic states and so is not block diagonal in the electronic states. In practice, authors who claim to be using $\boldsymbol{R}$ in their formulations usually ignore any matrix elements which they find inconvenient such as those of L_x and L_y. We shall return to this point in more detail later in this chapter.

7.4.3. Hougen's isomorphic Hamiltonian

There is a particular difficulty in the formulation of the full Hamiltonian for a linear molecule (and hence for a diatomic molecule) which was first identified by Hougen [15]. The source of this difficulty is the fact that only two rotational coordinates are required to define the orientation of a diatomic molecule in laboratory space, the Euler

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angles ϕ and θ. It is customary to define the molecule-fixed z axis to point along the diatomic molecule axis from nucleus 1 to nucleus 2. Without any loss of generality, we can take the third Euler angle χ to be zero so that the transformation of the coordinates R_i of a particle i in the space-fixed system to the coordinates of the same particle in the rotating system is given by

$$\begin{bmatrix} x_i' \\ y_i' \\ z_i' \end{bmatrix} = \begin{bmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{bmatrix} \begin{bmatrix} X_i \\ Y_i \\ Z_i \end{bmatrix}. \tag{7.88}$$

Using standard methods to transform differential operators, Hougen attempted to achieve as great a separation of electronic, vibrational, rotational and spin coordinates as possible. The resultant operator representing the rotational kinetic energy has the form

$$\mathcal{H}_{\text{rot}} = \frac{\hbar^2}{2\mu R^2}\left[(\mathcal{J}_{x'} - W_{x'})^2 + \frac{1}{\sin\theta}(\mathcal{J}_{y'} - W_{y'})\sin\theta(\mathcal{J}_{y'} - W_{y'})\right]. \tag{7.89}$$

The angular momentum operator $\mathcal{J}$ which emerges from this treatment has the form:

$$\boldsymbol{i}\hbar\mathcal{J}_{x'} + \boldsymbol{j}\hbar\mathcal{J}_{y'} + \boldsymbol{k}\hbar\mathcal{J}_{z'} = \boldsymbol{i}(\cot\theta\hbar W_{z'} - \operatorname{cosec}\theta p_\phi) + \boldsymbol{j}p_\theta + \boldsymbol{k}\hbar W_{z'}, \tag{7.90}$$

where $\hbar\boldsymbol{W}$ represents all the angular momenta apart from that due to the rotation of the nuclei:

$$\boldsymbol{W} = \boldsymbol{L} + \boldsymbol{S}, \tag{7.91}$$

and

$$p_\theta = -\mathrm{i}\hbar(\partial/\partial\theta), \tag{7.92}$$

$$p_\phi = -\mathrm{i}\hbar(\partial/\partial\phi). \tag{7.93}$$

The operators $\mathcal{J}_{x'}$, $\mathcal{J}_{y'}$ and $\mathcal{J}_{z'}$ are the instantaneous components of the total angular momentum in the molecule-fixed axis system, including nuclear, electron orbital and spin motion, as computed by an observer fixed in space (what Van Vleck calls the components *referred* to the molecule-fixed axis system). They are not, however, what one might naively expect from a knowledge of elementary angular momentum theory. Because of the absence of the third Euler angle in the rotational variables for a diatomic molecule, the components referred to the rotating axis system do not obey the usual commutation relations for angular momenta components (even though the space-fixed components $\mathcal{J}_X$, $\mathcal{J}_Y$ and $\mathcal{J}_Z$ do behave normally). Instead, the commutation relations are more complicated:

$$[\mathcal{J}_{x'}, \mathcal{J}_{y'}] = -\mathrm{i}\cot\theta\mathcal{J}_{x'} - \mathrm{i}\,W_z, \tag{7.94}$$

$$[\mathcal{J}_{y'}, \mathcal{J}_{z'}] = [\mathcal{J}_{z'}, \mathcal{J}_{x'}] = 0, \tag{7.95}$$

$$[\mathcal{J}_{x'}, W_{y'}] = \mathrm{i}\cot\theta\sum_k \varepsilon_{z'jk}W_k, \tag{7.96}$$

$$[\mathcal{J}_{y'}, W_j] = 0, \tag{7.97}$$

$$[\mathcal{J}_{z'}, W_j] = \mathrm{i}\sum_k \varepsilon_{z'jk}W_k, \tag{7.98}$$

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where $i, j, k = x', y'$ or z' and ε_{ijk} is equal to +1 if $ijk = x'y'z'$ or any cyclic permutation, equals -1 if any pair of these $x'y'z'$ are interchanged, and equals zero for any other combination. The components of $\boldsymbol{W}$ (or $\boldsymbol{L}$ and $\boldsymbol{S}$ separately) in the molecule-fixed axis system obey the normal commutation relations:

$$[W_i, W_j] = \mathrm{i} \sum_k \varepsilon_{ijk} W_k. \tag{7.99}$$

Thus we see that the operator $\mathcal{J}$ is not strictly an angular momentum operator in the quantum mechanical sense, which is why we have assigned it a different symbol. More importantly for the present purposes, we cannot use the armoury of angular momentum theory and spherical tensor methods to construct representations of the molecular Hamiltonian. In addition, the rotational kinetic energy operator, equation (7.89), takes a more complicated form than it has for a nonlinear molecule where there are three Euler angles (rotational coordinates).

This lack of a third Euler angle, which might at the outset have seemed to be a simplification, therefore turns out to be something of a nuisance. In order to avoid this problem, Hougen devised a construct which permitted the re-introduction of the Euler angle χ in the description of the rotational motion of a linear molecule; he called the resulting operator the *isomorphic Hamiltonian* [15]. Since this Hamiltonian has one more degree of freedom than the true Hamiltonian, it has additional eigenstates which are not eigenstates of the true Hamiltonian. However, it is simple to use a restricted set of basis states to diagonalise the isomorphic Hamiltonian so that these extra eigenstates are excluded.

To obtain the isomorphic Hamiltonian for a diatomic molecule, χ is introduced as an independent variable and the coordinates of the particles which make up the molecule are measured in an axis system (x, y, z) whose orientation is described by the Euler angles (ϕ, θ, χ) in the (X, Y, Z) axis system. We recall that we chose χ to be zero in constructing the true Hamiltonian. The (x, y, z) axes are therefore obtained by rotation of the (x', y', z') axis system about the $z'(= z)$ axis through the angle χ. As a result, we have

$$(J_x - W_x) = \cos\chi(J_{x'} - W_{x'}) + \sin\chi(J_{y'} - W_{y'}), \tag{7.100}$$

$$(J_y - W_y) = -\sin\chi(J_{x'} - W_{x'}) + \cos\chi(J_{y'} - W_{y'}), \tag{7.101}$$

$$(J_z - W_z) = (J_{z'} - W_{z'}) = 0. \tag{7.102}$$

The components of $\boldsymbol{J}$ referred to the new coordinate system then have completely standard definitions:

$$\hbar J_x = \cos\chi\left(\cot\theta p_\chi - \mathrm{cosec}\theta p_\phi\right) + \sin\theta p_\theta, \tag{7.103}$$

$$\hbar J_y = -\sin\chi\left(\cot\theta p_\chi - \mathrm{cosec}\theta p_\phi\right) + \cos\chi p_\theta, \tag{7.104}$$

$$\hbar J_z = p_\chi. \tag{7.105}$$

These components are now independent of the orbital and spin variables and so commute with $\boldsymbol{L}$ and $\boldsymbol{S}$. They also obey the commutation relations for a general angular momentum, provided only that the anomalous sign of i is used.

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In the isomorphic Hamiltonian, the rotational kinetic energy operator has the simpler (and familiar) form

$$\begin{aligned}\mathcal{H}_{\rm rot}^{\rm iso} &= \frac{\hbar^2}{2\mu R^2}[(J_x - W_x)^2 + (J_y - W_y)^2] \\ &= hcB(\boldsymbol{J} - \boldsymbol{W})^2. \end{aligned} \tag{7.106}$$

The second line of this equation follows from (7.102) above. We note that the awkward $\sin\theta$ factors in (7.89) have now disappeared. As Hougen points out, the eigenfunctions of the true Hamiltonian involve one less variable and so one less quantum number than the eigenfunctions of the artificial Hamiltonian and consequently the two operators cannot be completely isomorphic. However, a simple restriction on the extra quantum number in the artificial problem identifies that part of the full artifical Hamiltonian which *is* isomorphic with the true operator. Since the isomorphic Hamiltonian commutes with $(J_z - W_z)$, the two operators have a set of simultaneous eigenfunctions. Equation (7.102) states that only those eigenfunctions of the isomorphic Hamiltonian which have an eigenvalue of zero for $(J_z - W_z)$ are eigenfunctions of the true Hamiltonian.

Hougen's construct thus provides considerable simplification of the theory of the general linear molecule and has been used, often unknowingly, by countless authors. We use it with gratitude throughout this book.

7.4.4. Fine structure terms: spin–orbit, spin–spin and spin–rotation operators

In section 7.4.2 we dealt with perhaps the simplest contribution to the effective Hamiltonian for a particular electronic state, that of the rotational kinetic energy. We now turn our attention to contributions which are only slightly more complicated, the so-called fine structure interactions involving the electron spin angular momentum $\boldsymbol{S}$. Obviously for $\boldsymbol{S}$ to be non-zero, the molecule must be in an open shell electronic state with a general multiplicity $(2S + 1)$.

The terms in the fundamental Hamiltonian given in equation (7.71) which are involved are $\mathcal{H}_{\rm rot}$, $\mathcal{H}_{\rm so}^{\rm (e)}$, $\mathcal{H}_{\rm so}^{\rm (n)}$ and $\mathcal{H}_{\rm ss}^{\rm (tensor)}$. The first-order contributions can be written down directly from equation (7.43) as

$$\begin{aligned}\mathcal{H}_{\rm eff}^{(1)} = hcP_0\big\{&A^{(1)}(R)\mathrm{T}^1_{q=0}(\boldsymbol{L})\mathrm{T}^1_{q=0}(\boldsymbol{S}) + B^{(1)}(R)\mathrm{T}^1(\boldsymbol{J}-\boldsymbol{S})\cdot\mathrm{T}^1(\boldsymbol{J}-\boldsymbol{S}) \\ &+ \gamma^{(1)}(R)\mathrm{T}^1(\boldsymbol{J}-\boldsymbol{S})\cdot\mathrm{T}^1(\boldsymbol{S}) + (2\sqrt{6}/3)\lambda^{(1)}(R)\mathrm{T}^2_{q=0}(\boldsymbol{S},\boldsymbol{S})\big\}P_0 \end{aligned} \tag{7.107}$$

with the linear molecule restriction

$$\mathrm{T}^1_{q=0}(\boldsymbol{J} - \boldsymbol{L} - \boldsymbol{S}) = 0. \tag{7.108}$$

We recall that the component q is referred to the molecule-fixed axis system. The

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first-order contribution to the spin–orbit interaction involves $\mathcal{H}_{\rm so}^{\rm (e)}$,

$$A^{(1)}(R) = \frac{1}{hc\Lambda\Sigma}\langle \eta, \Lambda(S), \Sigma; R|\mathcal{H}_{\rm so}^{\rm (e)}|\eta, \Lambda(S), \Sigma; R\rangle, \tag{7.109}$$

where the quantum number product in the denominator is just the expectation value of $\mathrm{T}^1_{q=0}(\boldsymbol{L})\mathrm{T}^1_{q=0}(\boldsymbol{S})$. The first-order contribution to the spin–rotation interaction on the other hand involves $\mathcal{H}_{\rm so}^{\rm (n)}$:

$$\gamma^{(1)}(R) = -\frac{g_S e^2 B(R)}{4\pi\varepsilon_0 m_e c^2 S(S+1)} \times \langle \eta, \Lambda(S), \Sigma; R|\sum_{i,\alpha}(\boldsymbol{S}\cdot\boldsymbol{s}_i)Z_\alpha r_{i\alpha}^{-3}(z_i - z_\alpha)z_\alpha|\eta, \Lambda(S), \Sigma; R\rangle. \tag{7.110}$$

Here, as elsewhere, the subscripts i and α stand for electrons and nuclei respectively. The factor $(\boldsymbol{S}\cdot\boldsymbol{s}_i)/S(S+1)$ is used to project the contribution from each open shell electron i onto the total spin angular momentum $\boldsymbol{S}$. We remind ourselves that the effective Hamiltonian is constructed to operate within an electronic state with a given multiplicity $(2S+1)$.

The first-order contribution to the spin–spin coupling term involves just the expectation value of $\mathcal{H}_{\rm ss}^{\rm (tensor)}$:

$$\lambda^{(1)}(R) = \frac{1}{hc}\frac{\langle \eta, \Lambda(S), \Sigma; R|\mathcal{H}_{\rm ss}^{\rm (tensor)}|\eta, \Lambda(S), \Sigma; R\rangle}{(2/3)\{3\Sigma^2 - S(S+1)\}}. \tag{7.111}$$

Once again, the quantum numbers in brackets in the denominator are there simply to produce the correct matrix element, so that equation (7.79) is satisfied. Since the spin operators act on the spin coordinates only, the diagonal matrix element of the operator in $\mathcal{H}_{\rm eff}^{(1)}$, equation (7.107), is

$$\begin{aligned}\langle S, \Sigma|\mathrm{T}^2_{q=0}(\boldsymbol{S}, \boldsymbol{S})|S, \Sigma\rangle &= \langle S, \Sigma|(1/\sqrt{6})\left(3S_z^2 - \boldsymbol{S}^2\right)|S, \Sigma\rangle \\ &= (1/\sqrt{6})[3\Sigma^2 - S(S+1)].\end{aligned} \tag{7.112}$$

The last contribution in equation (7.107) is the first-order rotational kinetic energy, which we have already dealt with in section 7.4.2.

We now turn our attention to the second-order contributions. In order to see how these are derived, let us consider in particular the contributions of the spin–orbit interaction, $\mathcal{H}_{\rm so}^{\rm (e)}$. Before we can use second-order perturbation theory to evaluate these contributions, we need to write down the general matrix elements of this operator. We can do this easily if we write the expression in equation (7.72) in the simplified form

$$\mathcal{H}_{\rm so}^{\rm (e)} = \sum_i a_i(R)\mathrm{T}^1(\boldsymbol{l}_i)\cdot\mathrm{T}^1(\boldsymbol{s}_i), \tag{7.113}$$

where the summation is over all open shell electrons and $\hbar\boldsymbol{l}_i$ represents the orbital angular momentum of an individual electron i. It requires some work to show that this form of the spin–orbit operator, known as the microscopic form, is almost exactly equivalent to the full expression in equation (7.72); it neglects only the spin–other-orbit interactions between unpaired electrons [16]. However, all we need to accept at this

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stage is that the matrix elements of (7.113) obey exactly the same selection rules as those of (7.72). We can then evaluate the matrix elements of (7.113) in a Hund's case (a) representation by standard spherical tensor methods:

$$\langle \eta, \Lambda; S, \Sigma|\mathcal{H}_{\rm so}^{(\rm e)}|\eta', \Lambda'; S', \Sigma'\rangle = \sum_q (-1)^q \sum_i \langle \eta, \Lambda|a_i \mathrm{T}^1_{-q}(\boldsymbol{l}_i)|\eta', \Lambda'\rangle \langle S, \Sigma|\mathrm{T}^1_q(\boldsymbol{s}_i)|S', \Sigma'\rangle. \quad (7.114)$$

By the Wigner–Eckart theorem,

$$\langle S, \Sigma|\mathrm{T}^1_q(\boldsymbol{s}_i)|S', \Sigma'\rangle = (-1)^{S-\Sigma}\begin{pmatrix} S & 1 & S' \\ -\Sigma & q & \Sigma' \end{pmatrix}\langle S\|\mathrm{T}^1(\boldsymbol{s}_i)\|S'\rangle. \quad (7.115)$$

Hence

$$\langle \eta, \Lambda; S, \Sigma|\mathcal{H}_{\rm so}^{(\rm e)}|\eta', \Lambda'; S', \Sigma'\rangle = \sum_q (-1)^q (-1)^{S-\Sigma}\begin{pmatrix} S & 1 & S' \\ -\Sigma & q & \Sigma' \end{pmatrix} \sum_i \langle \eta, \Lambda|a_i \mathrm{T}^1_{-q}(\boldsymbol{l}_i)|\eta', \Lambda'\rangle \langle S\|\mathrm{T}^1(\boldsymbol{s}_i)\|S'\rangle. \quad (7.116)$$

The selection rules of $\mathcal{H}_{\rm so}^{(\rm e)}$ for Hund's case (a) quantum numbers can be seen immediately from this equation: $\Delta S = 0, \pm 1$ (by the triangle rule), $\Delta\Lambda = 0, \pm 1$, $\Delta\Sigma = 0, \mp 1$ so that $\Delta\Omega = 0$ where $\Omega = \Lambda + \Sigma$.

The second-order contribution of the spin–orbit coupling can now be written down using the expression in equation (7.43), namely:

$$\mathcal{H}^{(2)} = P_0 \Bigg\{ \sum_{\eta'\Lambda'} \sum_{S'\Sigma'} (V_{\eta\Lambda}(R) - V_{\eta'\Lambda'}(R))^{-1} \Bigg[\sum_q (-1)^q (-1)^{S-\Sigma} \begin{pmatrix} S & 1 & S' \\ -\Sigma & q & \Sigma' \end{pmatrix} \times \sum_i \langle S\|\mathrm{T}^1(\boldsymbol{s}_i)\|S'\rangle \langle \eta, \Lambda|\mathrm{T}^1_{-q}(a_i \boldsymbol{l}_i)|\eta', \Lambda'\rangle \Bigg] \Bigg[\sum_{q'} (-1)^{q'} (-1)^{S'-\Sigma'} \times \begin{pmatrix} S' & 1 & S \\ -\Sigma' & q' & \Sigma'' \end{pmatrix} \sum_j \langle S'\|\mathrm{T}^1(\boldsymbol{s}_j)\|S\rangle \langle \eta', \Lambda'|\mathrm{T}^1_{-q'}(a_j \boldsymbol{l}_j)|\eta, \Lambda''\rangle \Bigg] \Bigg\} P_0. \quad (7.117)$$

Only the unpaired electrons contribute to the sums over i and j because only these electrons contribute to the total spin. The operator that represents this contribution in the effective Hamiltonian is designed to act only within the manifold of the state of interest, $|\eta, S\rangle$. In other words, it should not make any explicit reference to the quantum numbers S' and Σ' which must therefore be suppressed. With this in mind, the pair of 3-j symbols in equation (7.117) which both include S' and Σ', can be re-expressed by making use of the relationship

$$\begin{pmatrix} j_1 & \ell_2 & \ell_3 \\ m_1 & \mu_2 & -\mu_3 \end{pmatrix}\begin{pmatrix} \ell_1 & j_2 & \ell_3 \\ -\mu_1 & m_2 & \mu_3 \end{pmatrix} = (-1)^p \sum_{j_3, m_3} (2j_3 + 1)\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \times \begin{pmatrix} \ell_1 & \ell_2 & j_3 \\ \mu_1 & -\mu_2 & m_3 \end{pmatrix}\begin{Bmatrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \ell_3 \end{Bmatrix}, \quad (7.118)$$

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where $p = \ell_1 + \ell_2 + \ell_3 + \mu_1 + \mu_2 + \mu_3$. Anticipating from equation (7.107) an operator which is diagonal in the quantum numbers Λ and Σ, we set $\Lambda'' = \Lambda$ and $\Sigma'' = \Sigma$ to obtain the general second-order contribution

$$\begin{aligned}\mathcal{H}^{(2)} = P_0 \Bigg\{ & \sum_{\eta',\Lambda'} \sum_{S',\Sigma'} (V_{\eta,\Lambda}(R) - V_{\eta',\Lambda'}(R))^{-1} (-1)^{S-\Sigma} \sum_k (2k+1) \begin{pmatrix} S & k & S \\ -\Sigma & 0 & \Sigma \end{pmatrix} \\ & \times (-1)^{2S'} \begin{Bmatrix} S & 1 & S' \\ 1 & S & k \end{Bmatrix} \sum_{i,j} \langle S \| \mathrm{T}^1(\boldsymbol{s}_i) \| S' \rangle \langle S' \| \mathrm{T}^1(\boldsymbol{s}_j) \| S \rangle \sum_q \begin{pmatrix} 1 & k & 1 \\ -q & 0 & q \end{pmatrix} \\ & \times \langle \eta, \Lambda | \mathrm{T}^1_{-q}(a_i \boldsymbol{l}_i) | \eta', \Lambda' \rangle \langle \eta', \Lambda' | \mathrm{T}^1_q(a_j \boldsymbol{l}_j) | \eta, \Lambda \rangle \Bigg\} P_0. \end{aligned} \tag{7.119}$$

The rank k can take values 0, 1 and 2 by the triangle rule. Of these, the scalar term with $k = 0$ has no Σ dependence and hence does not affect the relative positions of the ro-vibrational energy levels. It just makes a small contribution to the electronic energy of the state $|\eta, \Lambda\rangle$. The first-rank term produces a second-order contribution to the spin–orbit interaction because it is directly proportional to the quantum number Σ from the 3-j symbol in the first line of (7.119). The contribution to the spin–orbit parameter $A(R)$ which arises in this way is given (in cm^{-1}) by

$$\begin{aligned} A^{(2)}(R) = & \frac{1}{hc\Lambda[S(S+1)(2S+1)]^{1/2}} \sum_{\eta',\Lambda'} \sum_{S'} (V_{\eta,\Lambda}(R) - V_{\eta',\Lambda'}(R))^{-1} 3(-1)^{2S'} \\ & \times \begin{Bmatrix} S & 1 & S' \\ 1 & S & 1 \end{Bmatrix} \sum_{i,j} \langle S \| \mathrm{T}^1(\boldsymbol{s}_i) \| S' \rangle \langle S' \| \mathrm{T}^1(\boldsymbol{s}_j) \| S \rangle \sum_q \begin{pmatrix} 1 & 1 & 1 \\ -q & 0 & q \end{pmatrix} \\ & \times \langle \eta, \Lambda | \mathrm{T}^1_{-q}(a_i \boldsymbol{l}_i) | \eta', \Lambda' \rangle \langle \eta', \Lambda' | \mathrm{T}^1_q(a_j \boldsymbol{l}_j) | \eta, \Lambda \rangle. \end{aligned} \tag{7.120}$$

If $\Lambda = 0$, we know that this contribution must vanish because there is no direct spin–orbit coupling for a Σ state. This expected result can be proved by replacing q by $-q$ in equation (7.119). The effect of this replacement is to multiply the whole expression by $(-1)^k$. Thus the summation over q causes the $k = 1$ term to vanish for Σ states.

The third contribution from equation (7.119), that with $k = 2$, can be written as

$$\begin{aligned} \mathcal{H}^{(2)}_{\mathrm{ss}} = (-1)^{S-\Sigma} & \begin{pmatrix} S & 2 & S \\ -\Sigma & 0 & \Sigma \end{pmatrix} P_0 \Bigg\{ \sum_{\eta',\Lambda'} \sum_{S'} (V_{\eta,\Lambda}(R) - V_{\eta',\Lambda'}(R))^{-1} 5 \begin{Bmatrix} S & 1 & S' \\ 1 & S & 2 \end{Bmatrix} \\ & \times \sum_{i,j} \langle S \| \mathrm{T}^1(\boldsymbol{s}_i) \| S' \rangle \langle S' \| \mathrm{T}^1(\boldsymbol{s}_j) \| S \rangle \sum_q \begin{pmatrix} 1 & 2 & 1 \\ -q & 0 & q \end{pmatrix} \langle \eta, \Lambda | \mathrm{T}^1_{-q}(a_i \boldsymbol{l}_i) | \eta', \Lambda' \rangle \\ & \times \langle \eta', \Lambda' | \mathrm{T}^1_q(a_j \boldsymbol{l}_j) | \eta, \Lambda \rangle \Bigg\} P_0. \end{aligned} \tag{7.121}$$

This result now has exactly the same form as the first-order contribution to the spin–spin coupling term in equation (7.107) with the term in braces being equated with $(2/3)\sqrt{6}\lambda^{(2)} \langle S \| \mathrm{T}^2(\boldsymbol{S}, \boldsymbol{S}) \| S \rangle$ to ensure this result.

In a similar manner, there is a second-order contribution to the spin–rotation parameter which arises from the cross-term between the spin–orbit coupling and the

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rotational kinetic energy. We do not go through the details, but merely quote the result:

$$\gamma^{(2)}(R) = -2\sum_{\eta'}{}' \frac{M_1 + M_2}{[\{V_\eta(R) - V_{\eta'}(R)\}\langle S, \Sigma|S_-|S, \Sigma+1\rangle]}, \tag{7.122}$$

where

$$\begin{aligned} M_1 &= \langle \eta, \Lambda(S), \Sigma; R|B(R)L_-|\eta', \Lambda+1(S), \Sigma; R\rangle \\ &\quad \times \langle \eta', \Lambda+1(S), \Sigma; R|\mathcal{H}_{\rm so}^{\rm (e)}|\eta, \Lambda(S), \Sigma+1; R\rangle, \\ M_2 &= \langle \eta, \Lambda(S), \Sigma; R|\mathcal{H}_{\rm so}^{\rm (e)}|\eta', \Lambda-1(S), \Sigma+1; R\rangle \\ &\quad \times \langle \eta', \Lambda-1(S), \Sigma+1; R|B(R)L_-|\eta, \Lambda(S), \Sigma+1; R\rangle. \end{aligned} \tag{7.123}$$

In summary, we can write down the effective Hamiltonian which represents the fine-structure terms for a diatomic molecule in a $^{2S+1}\Lambda$ state as:

$$\begin{aligned} &\mathcal{H}_{\rm eff}(R) \\ &= hcP_0\big\{V_\eta^{\rm (ad)}(R) + V_\eta^{(sp)}(R) + A(R)\mathrm{T}^1_{q=0}(\boldsymbol{L})\mathrm{T}^1_{q=0}(\boldsymbol{S}) + B(R)\mathrm{T}^1(\boldsymbol{J}-\boldsymbol{S})\cdot\mathrm{T}^1(\boldsymbol{J}-\boldsymbol{S}) \\ &\quad + \gamma(R)\mathrm{T}^1(\boldsymbol{J}-\boldsymbol{S})\cdot\mathrm{T}^1(\boldsymbol{S}) + (2/3)\sqrt{6}\lambda(R)\mathrm{T}^2_{q=0}(\boldsymbol{S},\boldsymbol{S})\big\}P_0, \end{aligned} \tag{7.124}$$

where

$$A(R) = A^{(1)}(R) + A^{(2)}(R), \tag{7.125}$$

$$B(R) = B^{(1)}(R) + B^{(2)}(R), \tag{7.126}$$

$$\gamma(R) = \gamma^{(1)}(R) + \gamma^{(2)}(R), \tag{7.127}$$

$$\lambda(R) = \lambda^{(1)}(R) + \lambda^{(2)}(R). \tag{7.128}$$

In other words, each of the parameters is the sum of a first-order and a second-order contribution. We have met equation (7.126) for the effective rotational constant operator before, in an earlier section, where we pointed out that the second-order contribution $B^{(2)}$ is very much smaller than $B^{(1)}$ and that these two contributions have a different reduced mass dependence. It is important to realise that this is not generally true. Indeed, except for molecules with very light atoms such as H_2, the second-order contribution to the spin–rotation parameter is usually very much larger in magnitude than the first-order contribution. The same is also often true for the spin–spin coupling parameter λ. The reduced mass dependences of the two contributions to the spin–rotation parameter γ are different from each other and quite complicated. However, Brown and Watson [17] were able to show the rather remarkable result that when one takes the first- and second-order contributions together as in equation (7.127), the reduced mass dependence of the resultant parameter $\gamma(R)$ is simply μ^{-1}.

It will be noticed that two contributions to the vibrational potential energy, of the general form $V(R)$ and independent of the rotational and spin quantum numbers, have also been included in equation (7.124). These are corrections to $V_\eta(R)$, the zeroth-order contribution to the electronic energy defined in equation (7.76). The first term, $V_\eta^{\rm (ad)}(R)$, is the adiabatic contribution to the electronic energy, which we have discussed in section 2.7. It describes the first-order effect of the nuclear kinetic energy within the

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electronic state $|\eta, \Lambda\rangle$:

$$hcV_{\eta}^{(\mathrm{ad})}(R) = \langle \eta, \Lambda(S), \Sigma; R| \left\{ \frac{1}{2\mu} P_R^2 + hcB(R)\left(\boldsymbol{L}^2 - 2L_z^2\right) + \frac{1}{2M}\boldsymbol{P}^2 \right\} |\eta, \Lambda(S), \Sigma; R\rangle. \tag{7.129}$$

This is a relatively small contribution when compared with $V_\eta(R)$ but it is nevertheless important when considering the isotopic dependence of the electronic energy. The second term, $V_\eta^{(sp)}(R)$, describes the contribution from spin–spin coupling (in first order) and spin–orbit coupling (in second order) to the electronic energy:

$$hcV_{\eta}^{(sp)}(R) = \langle \eta, \Lambda(S), \Sigma; R|\mathfrak{H}_{\mathrm{ss}}^{(\mathrm{s})}|\eta, \Lambda(S), \Sigma; R\rangle + \frac{1}{2S+1}\sum_{\Sigma}\sum_{\eta', \Lambda', \Sigma'} \times \frac{|\langle \eta', \Lambda'(S'), \Sigma'; R|\mathfrak{H}_{\mathrm{so}}^{(\mathrm{e})}|\eta, \Lambda(S), \Sigma; R\rangle|^2}{[V_\eta(R) - V_{\eta'}(R)]}. \tag{7.130}$$

The second of these contributions is just the $k = 0$ contribution to the energy in equation (7.119). Neither of the contributions shows any dependence on the spin quantum number Σ.

7.4.5. Λ-doubling terms for a Π electronic state

The two component states of orbital degeneracy in a diatomic molecule have opposite parity. As we described in chapter 6, parity is the symmetry label associated with the behaviour of a wave function under the space-fixed inversion operator E^*:

$$E^* f(X, Y, Z) = f(-X, -Y, -Z). \tag{7.131}$$

Under circumstances where this operation leaves the physical system invariant, the quantum states have either positive or negative parity,

$$E^*\psi(X, Y, Z) = \pm\psi(X, Y, Z), \tag{7.132}$$

that is, they transform with the upper or lower sign choice in the above equation.

The two-fold degeneracy of these orbital levels is exact for the non-rotating molecule (strictly we have to consider spin–orbit levels: those with $\Omega \geq 1/2$ are degenerate for a non-rotating molecule). However, when the molecule rotates, the degeneracy is lifted in a manner which increases as J increases. The precise J dependence depends on the Ω value for Hund's case (a) states or on the Λ value for case (b). The phenomenon is known as lamda-doubling. All lamda-doubling effects originate from the admixture of the rotational levels of the degenerate electronic state with the corresponding levels of a Σ electronic state. Since each of these Σ state levels is non-degenerate, each has a particular parity, either positive or negative. Each therefore interacts with only *one* of the two degenerate components, namely, that with the same parity. This component is therefore shifted either up or down, away from its partner with the opposite parity.

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In this way, a splitting of the Λ-doublets arises. Λ-doubling can be described very succinctly by the effective Hamiltonian method.

For reasons which will become clear later, Λ-doubling effects are largest for molecules in Π electronic states. The electronic orbital part of the wave function for such a state can be represented by the pair of functions $|\Lambda = +1\rangle$ and $|\Lambda = -1\rangle$, which correspond to the angular momentum vector precessing in clockwise and anticlockwise directions about the internuclear axis. We shall instead take sum and difference combinations of these functions, $(1/\sqrt{2})\{|\Lambda = +1\rangle \pm |\Lambda = -1\rangle\}$, since they reflect the parity properties of the two Λ-doublets more closely (although they are still not true representations of states with a definite parity because we have not included the rotational and electron spin parts of the wave function). In the effective Hamiltonian, the Λ-doubling effects arise from the perturbations by the matrix elements of the spin–orbit and rotational Hamiltonians, $\mathcal{H}_{\rm so}$ and $\mathcal{H}_{\rm rot}$, with $\Delta\Lambda = \pm 1$. In second-order perturbation theory, these operators are applied twice giving rise to two types of term in the effective Hamiltonian, those with $\Delta\Lambda = 0$ overall and those with $\Delta\Lambda = \pm 2$. The former type makes equal contributions of the same sign to both Λ-doublets; Λ-doubling is not resolved by this type of term. On the other hand, the terms with $\Delta\Lambda = \pm 2$ make equal contributions of opposite sign to each Λ-doublet. These are then the terms which are responsible for Λ-doubling effects.

As mentioned above, the terms which are responsible for the coupling of the ${}^{2S+1}\Pi$ state to the ${}^{2S+1}\Sigma$ states are the spin–orbit coupling and the rotational electronic Coriolis term. Thus in the second-order perturbation expression in equation (7.43), the perturbation term is

$$\mathcal{H}' = \mathcal{H}_{\rm so} + \mathcal{H}_{\rm rot}, \tag{7.133}$$

where, for the present purposes, we only need consider the terms with $\Delta\Lambda = \pm 1$:

$$\mathcal{H}_{\rm so} = {\sum_{q=\pm 1}}' (-1)^q \mathrm{T}^1_q(a_i \boldsymbol{l}_i)\mathrm{T}^1_{-q}(\boldsymbol{s}_i), \tag{7.134}$$

$$\mathcal{H}_{\rm rot} = -2hc {\sum_{q=\pm 1}}' N_q \mathrm{T}^1_q(B\boldsymbol{L}). \tag{7.135}$$

The latter expression comes from equation (V.157). We recall that $\mathcal{H}_{\rm so}$ connects states with $\Delta S = 0, \pm 1$, whereas $\mathcal{H}_{\rm rot}$ couples in states of the same multiplicity only, $\Delta S = 0$.

In order to construct the Λ-doubling terms, we substitute the perturbation operator $\mathcal{H}'$ in the second-order expressions and look for terms which link the $|\eta, \Lambda = +1\rangle$ basis state with $|\eta, \Lambda = -1\rangle$. Because $\mathcal{H}'$ contains two independent operators, we finish up with three independent contributions to the effective Hamiltonian which are as follows:

(i) the squared term $\mathcal{H}_{\rm so} \times \mathcal{H}_{\rm so}$ which gives rise to an operator of the form $\mathrm{T}^1_q(\boldsymbol{S})\mathrm{T}^1_q(\boldsymbol{S})$,

(ii) the cross term $2 \times \mathcal{H}_{\rm so} \times \mathcal{H}_{\rm rot}$ which gives rise to an operator of the form $\mathrm{T}^1_q(\boldsymbol{S})\mathrm{T}^1_q(\boldsymbol{N})$,

(iii) the squared term $\mathcal{H}_{\rm rot} \times \mathcal{H}_{\rm rot}$ which gives rise to an operator of the form $\mathrm{T}^1_q(\boldsymbol{N})\mathrm{T}^1_q(\boldsymbol{N})$.

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In all of these expressions, the spherical tensor component q can take the values ± 1 only.

The operator terms in the effective Λ-doubling Hamiltonian can all be expressed more concisely by combining the spherical tensors from equation (7.135),

$$\mathrm{T}^2_{\pm 2}(\boldsymbol{A}, \boldsymbol{B}) = \mathrm{T}^1_{\pm 1}(\boldsymbol{A})\mathrm{T}^1_{\pm 1}(\boldsymbol{B}). \tag{7.136}$$

In this way, we arrive at the following effective Hamiltonian for Λ-doubling for a molecule in a $^{2S+1}\Pi$ state:

$$\mathcal{H}_{\mathrm{LD}}(R) = \sum_{q=\pm 1}{}' \exp(-2\mathrm{i}q\phi)\big[-o(R)\mathrm{T}^2_{2q}(\boldsymbol{S}, \boldsymbol{S}) + p(R)\mathrm{T}^2_{2q}(\boldsymbol{S}, \boldsymbol{N}) - q(R)\mathrm{T}^2_{2q}(\boldsymbol{N}, \boldsymbol{N})\big]. \tag{7.137}$$

The coordinate ϕ is the electron orbital azimuthal angle and the presence of the exponential factor $\exp(-2\mathrm{i}q\phi)$ ensures that only the matrix elements which connect the component $|\eta, \Lambda = +1\rangle$ with $|\eta, \Lambda = -1\rangle$ are non-zero. The electron orbital basis functions used in this book imply a choice of phase factor which leads to

$$\langle \eta, \Lambda = \pm 1| \exp(\pm 2\mathrm{i}\phi)|\eta, \Lambda = \mp 1\rangle = -1. \tag{7.138}$$

We see that for a molecule in a $^{2S+1}\Pi$ state, there are in general three Λ-doubling parameters. However, for a singlet state ($S = 0$), only q is non-zero and for a doublet state, p and q are non-zero. To second order in perturbation theory, these parameters are given by the following expressions (in cm^{-1}) :

$$o(R) = o^{(1)}(R) + o^{(2)}(R), \tag{7.139}$$

where

$$o^{(1)}(R) = -\left(\frac{6}{5}\right)^{1/2} g_S^2 \mu_B^2 (\mu_0/4\pi hc)[S(S+1)(2S+1)]^{-1} \begin{Bmatrix} S & 1 & S \\ 1 & S & 2 \end{Bmatrix}^{-1}$$
$$\times \sum_{i,j>i} \langle S\|\mathrm{T}^2(\boldsymbol{s}_i, \boldsymbol{s}_j)\|S\rangle \langle \eta, \Lambda = 1|C^2_2(\theta, \phi) r_{ij}^{-3}|\eta, \Lambda = -1\rangle, \tag{7.140}$$

$$o^{(2)}(R) = -(hc)^{-1}[S(S+1)(2S+1)]^{-1} \begin{Bmatrix} S & 1 & S \\ 1 & S & 2 \end{Bmatrix}^{-1}$$
$$\times \sum_{\eta', \Lambda'} \sum_{S'} (V_{\eta,\Pi}(R) - V_{\eta,\Sigma}(R))^{-1}(-1)^s \begin{Bmatrix} S & 1 & S' \\ 1 & S & 2 \end{Bmatrix} \sum_{i,j} \langle S\|\mathrm{T}^1(\boldsymbol{s}_i)\|S'\rangle \langle S'\|\mathrm{T}^1(\boldsymbol{s}_j)\|S\rangle$$
$$\times \langle \eta, \Lambda = 1|\mathrm{T}^1_1(a_i \boldsymbol{l}_i)|\eta', \Lambda' = 0^s\rangle \langle \eta', \Lambda' = 0^s|\mathrm{T}^1_{-1}(a_j \boldsymbol{l}_j)|\eta =, \Lambda = 1\rangle, \tag{7.141}$$

$$p(R) = -4[S(S+1)(2S+1)]^{-1/2} \sum_{\eta', \Lambda'} (V_{\eta,\Pi}(R) - V_{\eta,\Sigma}(R))^{-1}(-1)^s$$
$$\times \langle \eta, \Lambda = 1|B(R)\mathrm{T}^1_1(\boldsymbol{L})|\eta', \Lambda = 0^s\rangle \sum_i \langle \eta', \Lambda = 0^s|a_i \mathrm{T}^1_{-1}(\boldsymbol{l}_i)|\eta, \Lambda = 1\rangle$$
$$\times \langle S\|\mathrm{T}^1(\boldsymbol{s}_i)\|S\rangle, \tag{7.142}$$

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$$q(R) = 4hc \sum_{\eta',\Lambda'} (V_{\eta,\Pi}(R) - V_{\eta,\Sigma}(R))^{-1}(-1)^s |\langle \eta,\, \Lambda = 1|B(R)\mathrm{T}^1_1(\boldsymbol{L})|\eta',\, \Lambda = 0^s\rangle|^2. \tag{7.143}$$

These expressions apply for a state with total spin angular momentum S. The exponent s is even for Σ^+ states and odd for Σ^- states. The factorisation of the spin and orbital matrix elements in these expressions has been achieved by making a single configuration approximation. If configuration interaction is not negligible, more general expressions, given in a paper on the effective Hamiltonian by Brown, Colbourn, Watson and Wayne [7] are used. The Λ-doubling parameters p and q were originally introduced by Mulliken and Christy [18].

The expressions in equations (7.139) to (7.143) are exact to second order in perturbation theory. There are also higher-order terms of the same operator form as given in (7.137) but such contributions are much smaller as long as the interaction terms are small compared with the separation of the Π and Σ states; this is usually the case. It is important to appreciate that the form of the Λ-doubling operator is the same even when these higher order effects are included. This is a real advantage of the effective Hamiltonian approach. The correct form of the Hamiltonian can be established by a limited perturbation treatment. Thus, no approximation is made in fitting the parameters of this Hamiltonian to experimental data. The limitations, such as they are, arise only when the parameters so determined are compared with theoretical expectations.

We note that the perturbation terms in the full Hamiltonian which are responsible for the Λ-doubling effects are the same as those which give rise to the spin–spin and spin–rotation terms as discussed in the previous section, namely $\mathcal{H}_{\mathrm{rot}}$ and $\mathcal{H}_{\mathrm{so}}$. The only difference is that we select the effective operators with $\Delta\Lambda = 0$ for the fine-structure terms and those with $\Delta\Lambda = \pm 2$ for the Λ-doubling terms. Because of this, the Λ-doubling effects manifest themselves in the second order of perturbation theory, that is, they depend on the admixture of Σ electronic states, whereas the fine-structure terms have both first- and second-order contributions, as given in equations (7.125) to (7.128). This is an important point to appreciate. In addition to terms in the effective Hamiltonian which have the same operator form as in the full Hamiltonian, there are others which have a completely different form. The common origin of the fine-structure and Λ-doubling effects in the effective Hamiltonian suggests that the two sets of parameters are related. These relationships can have a very simple form in particular circumstances. We shall discuss them after we have included the effects of vibrational averaging (over R) in the effective Hamiltonian.

7.4.6. Nuclear hyperfine terms

When a molecule contains an atom with a nuclear spin $I \geq 1/2$, its energy levels acquire an additional $(2I + 1)$ degeneracy. This degeneracy is lifted in practice by magnetic and electric interactions which are called nuclear hyperfine interactions; they have been described in detail in chapter 4. The magnitude of these interactions is usually relatively

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small, only rarely larger than 0.03 cm^{-1} or 1 GHz. The size of nuclear hyperfine effects is therefore very much less than electron spin fine structure effects, which in turn are smaller than the electronic and vibrational contributions to the energy. Consequently, it is usually only necessary to include the first-order effects of the nuclear hyperfine terms in the effective Hamiltonian.

We recall from chapter 4 that there are many individual types of interaction which involve the nuclear magnetic dipole and electric quadrupole moments. Let us take just three of these to exemplify how the effective Hamiltonian is constructed. They are as follows:

(i) the Fermi contact interaction

$$\mathcal{H}_{\mathrm{F}} = (2/3)\sum_{\alpha}\sum_{i} g_S \mu_B g_\alpha \mu_N \mu_0 \delta(\boldsymbol{r}_{\alpha i})\boldsymbol{s}_i \cdot \boldsymbol{I}_\alpha, \tag{7.144}$$

(ii) the dipole–dipole coupling term,

$$\mathcal{H}_{\mathrm{dip}} = -\sum_{\alpha}\sum_{i} g_S \mu_B g_\alpha \mu_N \frac{\mu_0}{4\pi}\left\{\frac{\boldsymbol{s}_i \cdot \boldsymbol{I}_\alpha}{\boldsymbol{r}_{\alpha i}^3} - \frac{3(\boldsymbol{s}_i \cdot \boldsymbol{r}_{\alpha i})(\boldsymbol{I}_\alpha \cdot \boldsymbol{r}_{\alpha i})}{r_{\alpha i}^5}\right\}, \tag{7.145}$$

(iii) the electric quadrupole coupling term,

$$\mathcal{H}_{\mathrm{Q}} = -e\sum_{\alpha} \mathrm{T}^2(\nabla \boldsymbol{E}_\alpha)\cdot \mathrm{T}^2(\boldsymbol{Q}_\alpha). \tag{7.146}$$

In these expressions the index i runs over electrons and α runs over nuclei. The Fermi contact term describes the magnetic interaction between the electron spin and nuclear spin magnetic moments when there is electron spin density at the nucleus. This condition is imposed by the presence of the Dirac delta function $\delta(\boldsymbol{r}_{\alpha i})$ in the expression. The dipole–dipole coupling term describes the classical interaction between the magnetic dipole moments associated with the electron and nuclear spins. It depends on the relative orientations of the two moments described in equation (7.145) and falls off as the inverse cube of the separations of the two dipoles. The cartesian form of the dipole–dipole interaction to some extent masks the simplicity of this term. Using the results of spherical tensor algebra from the previous chapter, we can bring this into the open as

$$\mathcal{H}_{\mathrm{dip}} = -(10)^{1/2}\sum_{\alpha}\sum_{i} g_S \mu_B g_\alpha \mu_N (\mu_0/4\pi)\mathrm{T}^1(\boldsymbol{I}_\alpha)\cdot \mathrm{T}^1(\boldsymbol{S}_i, \boldsymbol{C}_i). \tag{7.147}$$

In other words, it is a first-rank scalar product involving the nuclear spin angular momentum with an operator defined by

$$\mathrm{T}^1_q(\boldsymbol{S}_i, \boldsymbol{C}_i) = -(-1)^q \sum_{q_1,q_2} \mathrm{T}^1_{q_1}(\boldsymbol{s}_i) C^2_{q_2}(\theta_{\alpha i}, \phi_{\alpha i}) r_{\alpha i}^{-3} (3)^{1/2} \begin{pmatrix} 1 & 2 & 1 \\ q_1 & q_2 & -q \end{pmatrix}, \tag{7.148}$$

where $(r_{\alpha i}, \theta_{\alpha i}, \phi_{\alpha i})$ are the spherical polar coordinates of electron i relative to nucleus α. Finally, the quadrupole term describes the interaction between the electric quadrupole moment of nucleus α and the electric field gradient $\nabla \boldsymbol{E}_\alpha$ at the nucleus; the latter is made up of contributions from all nearby charges, both electrons and nuclei. This electric field gradient also falls off as $r_{\alpha i}^{-3}$.

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The first-order contribution of these hyperfine interactions to the effective electronic Hamiltonian involves the diagonal matrix elements of the individual operator terms over the electronic wave function, see equation (7.43). As before, we factorise out those terms which involve the electronic spin and spatial coordinates. For example, for the Fermi contact term we need to evaluate matrix elements of the type:

$$\langle \eta, \Lambda(S)|\delta(\boldsymbol{r}_{\alpha i})\boldsymbol{s}_i|\eta, \Lambda(S)\rangle. \tag{7.149}$$

The nuclear hyperfine operators therefore have essentially the same form in the effective Hamiltonian as they do in the full Hamiltonian, certainly as far as the nuclear spin terms are concerned. Throughout our derivation, we have assumed that the electronic state $|\eta, \Lambda\rangle$ which is to be described by our effective Hamiltonian has a well-defined spin angular momentum S. It is therefore desirable to write the effective Hamiltonian in terms of the associated operator $\boldsymbol{S}$ rather than the individual spin angular momenta $\boldsymbol{s}_i$. We introduce the projection operators Φ_i^s for each electron i,

$$\boldsymbol{s}_i = \Phi_i^s \boldsymbol{S}. \tag{7.150}$$

The operator can be evaluated by taking the scalar product of each side with $\boldsymbol{S}$ and rearranging to give

$$\Phi_i^s = \boldsymbol{s}_i \cdot \boldsymbol{S}/\{S(S+1)\}. \tag{7.151}$$

For a molecule in a Hund's case (a) state where the component of $\boldsymbol{S}$ along the z axis is well defined as Σ, we can write

$$\Phi_i^s = s_{iz}/\Sigma. \tag{7.152}$$

Using these results, we can write

$$\mathcal{H}_{\mathrm{F}}(R) = \sum_{\alpha} b_F^{\alpha} \boldsymbol{I}_{\alpha} \cdot \boldsymbol{S}, \tag{7.153}$$

where

$$b_{\mathrm{F}}^{\alpha} = \sum_i \frac{2g_S\mu_B g_{\alpha}\mu_N\mu_0}{3} \langle \eta, \Lambda(S)|\Phi_i^s \delta(\boldsymbol{r}_{\alpha i})|\eta, \Lambda(S)\rangle. \tag{7.154}$$

In a similar fashion, the dipole–dipole coupling term becomes

$$\mathcal{H}_{\mathrm{dip}}(R) = \sum_{\alpha} (\sqrt{6}/3) c^{\alpha} \mathrm{T}^2_{q=0}(\boldsymbol{I}_{\alpha}, \boldsymbol{S}), \tag{7.155}$$

where

$$c^{\alpha} = \sum_i \frac{3g_S\mu_B g_{\alpha}\mu_N\mu_0}{8\pi} \langle \eta, \Lambda(S)|\Phi_i^s (3\cos^2\theta_{i\alpha} - 1) r_{i\alpha}^{-3}|\eta, \Lambda(S)\rangle, \tag{7.156}$$

and the component $q = 0$ refers as always to the molecule-fixed z axis. We remember that the parameters b_{F} and c^{α} in equations (7.154) and (7.156) are still at this stage functions of the molecular bond length R, albeit weak ones.

Since the electric quadrupole interaction does not involve the electron spin operators, its form remains the same as in equation (7.146) with the operator $\mathrm{T}^2(\nabla \boldsymbol{E})$

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evaluated over the electronic wave function:

$$\langle \eta, \Lambda(S)|\mathrm{T}^2_{q=0}(\nabla \boldsymbol{E})|\eta, \Lambda(S)\rangle. \tag{7.157}$$

The effective operator is the product of one operator on three-dimensional spatial coordinates and another which acts on nuclear spin space. This distinction can be brought out even more clearly by making use of the operator replacement theorem in section 5.5.3 to give

$$\mathcal{H}_{\mathrm{Q}}(R) = \sum_{\alpha} \frac{eQ_\alpha q_0^\alpha}{4I_\alpha(2I_\alpha - 1)} \sqrt{6}\mathrm{T}^2_{q=0}(\boldsymbol{I}_\alpha, \boldsymbol{I}_\alpha). \tag{7.158}$$

The expectation value over the electric field gradient is represented by the parameter q_0^α:

$$q_0^\alpha = -2\langle \eta, \Lambda|\mathrm{T}^2_{q=0}(\nabla \boldsymbol{E})|\eta, \Lambda\rangle. \tag{7.159}$$

This parameter is also R-dependent at this stage of the development. We note the curiosity that, because of the way in which it is defined, the parameter actually represents the *negative* of the electric field gradient.

In equations (7.155) and (7.158) we have taken the diagonal $q = 0$ component of the second-rank spherical tensors $\mathrm{T}^2(\boldsymbol{I}_\alpha, \boldsymbol{S})$ and $\mathrm{T}^2(\boldsymbol{I}_\alpha, \boldsymbol{I}_\alpha)$. In general, these interactions and others like them will have off-diagonal terms also, with $q = \pm 1$ and ± 2. The $q = \pm 2$ components are particularly interesting because, for a molecule in a Π electronic state, they connect the $|\Lambda = +1\rangle$ and $|\Lambda = -1\rangle$ components directly. They therefore make additional hyperfine contributions to the Λ-doubling of molecules in Π electronic states. As a result, the nuclear hyperfine splitting of one component of a Λ-doublet is different from that of the other component. The two contributions are:

$$\mathcal{H}_{\mathrm{dip}}(R) = \sum_{\alpha} {\sum_{q=\pm 1}}' \exp(-2\mathrm{i}q\phi) d^\alpha \mathrm{T}^2_{2q}(\boldsymbol{I}_\alpha, \boldsymbol{S}), \tag{7.160}$$

$$\mathcal{H}_{\mathrm{Q}}(R) = -\sum_{\alpha} {\sum_{q=\pm 1}}' \exp(-2\mathrm{i}q\phi) \frac{eQ_\alpha q_2^\alpha}{4I_\alpha(2I_\alpha - 1)} \mathrm{T}^2_{2q}(\boldsymbol{I}_\alpha, \boldsymbol{I}_\alpha), \tag{7.161}$$

where

$$d^\alpha = \sum_i \frac{3g_S\mu_B g_\alpha \mu_N \mu_0}{8\pi} \langle \eta, \Lambda = \pm 1|\Phi_i^s \sin^2\theta_\alpha r_{i\alpha}^{-3}|\eta, \Lambda = \pm 1\rangle, \tag{7.162}$$

and

$$q_2^\alpha = -2\sqrt{6}\langle \eta, \Lambda = \pm 1|\mathrm{T}^2_{\pm 2}(\nabla_\alpha \boldsymbol{E})|\eta, \Lambda = \mp 1\rangle. \tag{7.163}$$

The other off-diagonal terms, with $q = \pm 1$, mix different electronic states with $\Delta\Lambda = \pm 1$. In the great majority of cases this mixing is too small to be significant, even with the most accurate measurements. However when the states involved happen to lie close together, or when the mixing term is unusually large, these off-diagonal effects produce additional higher-order terms in the effective Hamiltonian. We will not discuss these effects any further.

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7.4.7. Higher-order fine structure terms

Thus far, we have investigated the various contributions to the effective Hamiltonian for a diatomic molecule in a particular electronic state which arise from the spin–orbit and rotational kinetic energy terms treated up to second order in degenerate perturbation theory. Higher-order effects of such mixing will also contribute and we now consider some of their characteristics.

If we refer back to the explicit forms for third- and fourth-order contributions, given in equation (7.43) and depicted in figure 7.1, we see that the number of possible pathways between the various electronic states involved increases rapidly with the order of perturbation theory. This makes the mathematical treatment of such terms considerably more arduous and the work involved in going beyond fourth order renders the exercise futile. Fortunately, in the great majority of cases, these higher order contributions can be safely neglected. There are two reasons for this. First, the contributions get progressively smaller as the order of perturbation theory increases and second, there are angular momentum constraints on the effects of such terms.

The first of these reasons can be easily appreciated by reference to equation (7.43) again. It can be seen that the nth order terms have the general form $\langle i|\mathcal{H}'|j\rangle^n/(E_0 - E_i)^{n-1}$, that is, the successive orders of terms in the perturbation expansion are decreased by the factor $\langle i|\mathcal{H}'|j\rangle/(E_0 - E_i)$. If the perturbation treatment is well constructed from a convergence point of view, this factor will be considerably smaller than unity; for light molecules, it is typically on the order of 10^{-2}. Consequently, the higher-order effects become rapidly smaller and, for all but the most precise measurements, are negligible compared with the experimental uncertainty. The second consideration is more subtle but in the end more powerful because it depends on symmetry properties of the molecular system. It is related to the rank of the electron spin operator in the effective Hamiltonian. Though not always desirable, it is always possible to collect the various spin terms together and to express a typical term in the effective Hamiltonian as the scalar product

$$\mathrm{T}^k(\boldsymbol{X}) \cdot \mathrm{T}^k(\boldsymbol{S}), \tag{7.164}$$

where the operator $\boldsymbol{X}$ stands for the non-spin terms such as position $\boldsymbol{r}$, angular momentum $\boldsymbol{N}$ or orbital angular momentum $\boldsymbol{L}$. For a molecule in a state with a well-defined spin angular momentum S, simple application of the Wigner–Eckart theorem to the spin term leads to a 3-j symbol with upper row arguments S, k and S. We recall that such a symbol is subject to the triangle rule $\Delta(S, k, S)$. The matrix elements of the effective operator (7.164) within the electronic state of interest will therefore be rigorously zero unless $2S \geq k$. We have already met examples of this constraint in section 7.4.4. The spin–rotation term is first rank in electron spin and so appears in states of doublet or higher multiplicity. The spin–spin fine structure term is second rank and so only occurs in states of triplet or higher multiplicity. When the perturbation term involves the electron spin through spin–orbit coupling, the higher-order terms are of higher rank in the operator $\boldsymbol{S}$ and so their effects do not show up in states of lower multiplicity.

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Table 7.1. *Some higher-order contributions to the effective Hamiltonian*

Perturbation form	Parameter	Order of perturbation	Rank of spin operator
$(\boldsymbol{N}\cdot\boldsymbol{S})(\boldsymbol{L}\cdot\boldsymbol{S})(\boldsymbol{L}\cdot\boldsymbol{S})$	γ_S	3	3
$(L_z\cdot S_z)(\boldsymbol{L}\cdot\boldsymbol{S})(\boldsymbol{L}\cdot\boldsymbol{S})$	η	3	3
$(\boldsymbol{L}\cdot\boldsymbol{S})(\boldsymbol{L}\cdot\boldsymbol{S})(\boldsymbol{L}\cdot\boldsymbol{S})(\boldsymbol{L}\cdot\boldsymbol{S})$	Θ	4	4

In order to appreciate this point more clearly, we confine our attention to the contributions to $\mathcal{H}_{\rm eff}$ produced by perturbations from the spin–orbit coupling $\mathcal{H}_{\rm so}$ and the electronic Coriolis mixing $\mathcal{H}_{\rm rot}$. If we represent an off-diagonal matrix element of the former by $(\boldsymbol{L}\cdot\boldsymbol{S})$ and the latter by $(\boldsymbol{N}\cdot\boldsymbol{L})$, we can describe some examples of these higher order terms, as shown in table 7.1. The third-rank terms appear only in states of quartet or higher multiplicity and the fourth-rank terms in states of quintet (or higher) multiplicity. With the important exception of transition metal compounds, the vast majority of electronic states encountered in practice have triplet multiplicity or lower.

Let us consider the derivation of the higher-order spin–rotation term γ_S in more detail. The contribution of such a term to the energy levels of molecules in quartet states was first suggested by Hougen [19] and developed in detail by Brown and Milton [20]. The terms arise in the third order of perturbation theory, the general form of which is given in equation (7.43) and illustrated in figure 7.1. Two examples of the way in which these perturbations affect the levels of a $^4\Sigma$ state are shown in figure 7.2. In the first example, the admixture of a $^4\Pi$ state, the normalisation terms have to be written in a symmetrised form to ensure that the resulting operator is Hermitian. The second example of a $^2\Sigma$ state shows that states of different multiplicity can also contribute to these higher order effects. Using the same approach as that described for the fine structure terms in section 7.4.4 but with rather more algebra, we can obtain the following expression for the third-order spin–rotation effects,

$$\mathcal{H}_{\rm sr}^{(3)} = C^{(3)}(R)\mathrm{T}^3(\boldsymbol{L}^2,\boldsymbol{N})\cdot\mathrm{T}^3(\boldsymbol{S},\boldsymbol{S},\boldsymbol{S}), \tag{7.165}$$

where

$$\begin{aligned}
C^{(3)}(R) &= -(10)^{-1/2}\langle\Lambda|\mathrm{T}^2_0(\boldsymbol{L}^2)|\Lambda\rangle^{-1}\langle S\|\mathrm{T}^3(\boldsymbol{S},\boldsymbol{S},\boldsymbol{S})\|S\rangle^{-1}(35)\\
&\times\sum_{\eta',\Lambda',\Sigma',q}\left(E^0_\eta(R)-E^0_{\eta'}(R)\right)^{-2}(-1)^{q+S-\Sigma+S'-\Sigma}|\langle\eta,\Lambda,S\|\sum_i\mathrm{T}^1(\boldsymbol{s}_i)\mathrm{T}^1_q(a_i\boldsymbol{l}_i)\|\eta',\Lambda',S'\rangle|^2\\
&\times\begin{pmatrix}1 & 2 & 3\\ q & -q\pm1 & \mp1\end{pmatrix}\begin{Bmatrix}1 & S & S'\\ S & 2 & 3\end{Bmatrix}\\
&\times\begin{pmatrix}1 & 1 & 2\\ -q & \pm1 & q\mp1\end{pmatrix}[S(S+1)(2S+1)]^{1/2}\begin{Bmatrix}1 & S' & S\\ S & 1 & 2\end{Bmatrix}\\
&\times[B'(R)-B(R)],
\end{aligned} \tag{7.166}$$

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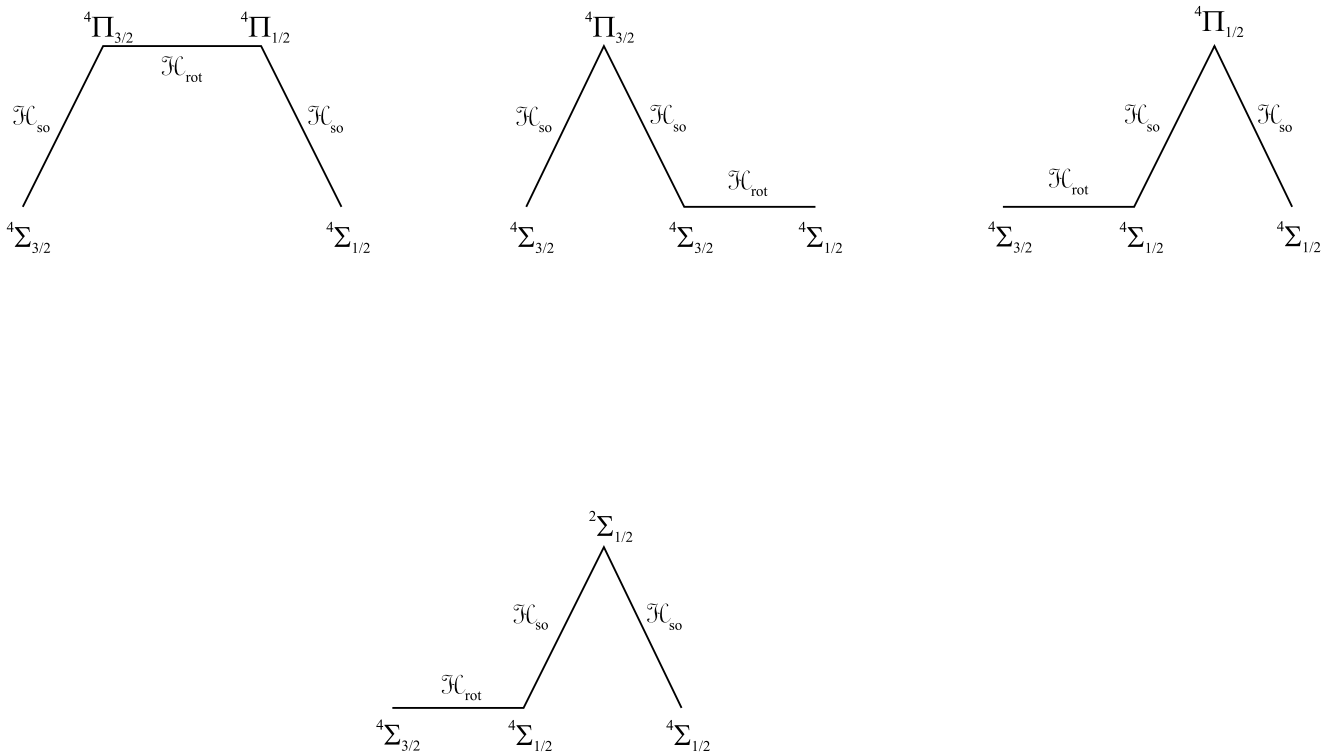

Figure 7.2. Diagrammatic representation of some third-order contributions to the matrix elements $\langle \Omega = 1/2|\mathcal{H}_{\text{eff}}|\Omega = 3/2\rangle$ in a $^4\Sigma$ state. The three top diagrams illustrate the admixture of $^4\Pi$ states, whilst the lower diagram shows the admixture of a $^2\Sigma$ state.

and

$$\langle S\|\mathrm{T}^3(\boldsymbol{S},\boldsymbol{S},\boldsymbol{S})\|S\rangle = (1/4)(10)^{-1/2}[(2S-2)(2S-1)(2S)(2S+1) \times (2S+2)(2S+3)(2S+4)]^{1/2}. \quad (7.167)$$

The parameter γ_S, first introduced by Brown and Milton [20], is related to $C^{(3)}(R)$ in equation (7.165) by

$$\gamma_S(R) = (6)^{1/2}(10)^{-1}C^{(3)}(R)\langle\eta,\Lambda|\mathrm{T}^2_0(\boldsymbol{L}^2)|\eta,\Lambda\rangle. \quad (7.168)$$

This expression for the higher-order spin–rotation interaction probably seems at best daunting and at worse cumbersome. However the great merit of the formulation in equation (7.165) is that it is very straightforward to work out its matrix elements, as we shall see later.

The experimental evidence for such a contribution to the spin–rotation interaction in the effective Hamiltonian was somewhat elusive in the early days although there are now well documented cases of its involvement, for example for CH in its $^4\Sigma^-$ state [21]. Equation (7.166) suggests one reason why this parameter is not as important in practice as might be expected. The last factor on the right-hand side of (7.166) is just the difference of the rotational constant operators for the upper and lower states. This causes a considerable degree of cancellation in a typical situation because the B value is not expected to vary markedly between the electronic states.

We shall not go through the details of the derivations of the other terms in table 7.1. Suffice it to say that they are similar to that described for the parameter $\gamma_S(R)$. We shall write down their operator form once we have dealt with the next stage of the development of the effective Hamiltonian, that of vibrational averaging.

7.5. Effective Hamiltonian for a single vibrational level

7.5.1. Vibrational averaging and centrifugal distortion corrections

Once we have removed the terms which couple different electronic states (at least to a certain level of accuracy), we can deal with the motion in the other degrees of freedom of the molecule for each electronic state separately. The next step in the process is to consider the vibrational degree of freedom which is usually responsible for the largest energy separations within each electronic state. If we perform a suitable transformation to uncouple the different vibrational states, we obtain an effective Hamiltonian for each vibronic state. Once again, we adopt a perturbation approach.

In this case, the zeroth-order Hamiltonian is chosen to represent the vibrational energy of the anharmonic oscillator:

$$\{P_R^2/2\mu + V_\eta(R)\}|\eta,v\rangle = |\eta,v\rangle hc\{T_{\eta e} + G^{(0)}_{\eta v}\}. \quad (7.169)$$

Here $|\eta,v\rangle$ is the radial eigenvector with vibrational quantum number v in the electronic state $|\eta,\Lambda\rangle$. It is assumed that the potential curve $V_\eta(R)$ has a minimum value $V_\eta(R_{\eta e})$ equal to $hcT_{\eta e}$ at the equilibrium bond length $R_{\eta e}$, i.e. this defines the energy origin of

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the electronic state in question. The zeroth-order vibrational term value relative to this minimum is then $G_{\eta v}^{(0)}$ where

$$G_{\eta v}^{(0)} = \left(v + \tfrac{1}{2}\right)\omega_{\eta e} - \left(v + \tfrac{1}{2}\right)^2 \omega_{\eta e} x_e + \left(v + \tfrac{1}{2}\right)^3 \omega_{\eta e} y_e + \cdots . \tag{7.170}$$

We recall that the vibrational potential energy function $V_\eta(R)$ is just the zeroth-order eigenvalue in the description of the electronic motion given in equation (7.76). Although this is not the most accurate choice we could make at this level (it is possible, for example, to add the adiabatic correction in equation (7.129)), it has the great advantage that it is isotopically independent. For heavier molecules, the spin correction term $V_\eta^{(\mathrm{sp})}(R)$ in equation (7.130) could be included without spoiling the isotopic independence but for lighter molecules we prefer to develop the Hamiltonian with a power series dependence on the spin operators. This is achieved by avoiding spin terms in the zeroth-order vibrational energies.

We use the operator on the left-hand side of equation (7.169) as the zeroth-order vibrational Hamiltonian. The remaining terms in the effective electronic Hamiltonian, given for example in equations (7.124) and (7.137), are treated as perturbations. In a similar vein to the electronic problem, we consider only first- and second-order corrections as given in equations (7.68) and (7.69) to produce an effective Hamiltonian $\mathcal{H}_{\eta v}$ which is confined to act within a single vibronic state $|\eta, v\rangle$ only. Once again, the condition for the validity of this approximation is that the perturbation matrix elements should be small compared with the vibrational intervals. It will therefore tend to fail for loosely bound states with low vibrational frequencies.

The first-order perturbation contribution is obtained by replacing each operator function $X(R)$ by its anharmonic expectation value,

$$X_{\eta v} = \langle \eta, v | X_\eta(R) | \eta, v \rangle = X_{\eta e} + (B_{\eta e}/\omega_{\eta e})(X''_{\eta e} - 3a_{1\eta} X'_{\eta e})(v + 1/2) + \cdots , \tag{7.171}$$

where X corresponds to any one of $V^{(\mathrm{ad})}$, $V^{(\mathrm{sp})}$, B, A, γ, λ, o, p, q or the nuclear hyperfine parameters. The expansion in powers of $(v + 1/2)$ can be obtained by a semi-classical perturbation treatment [22]. The subscripts η and e refer to the value at $R_{\eta e}$ and the derivatives are defined by

$$X'_{\eta e} = (\mathrm{d}X_\eta(R)/\mathrm{d}\xi)_{R_{\eta e}}, \quad X''_{\eta e} = (\mathrm{d}^2 X_\eta(R)/\mathrm{d}\xi^2)_{R_{\eta e}}, \tag{7.172}$$

where $\xi = (R - R_{\eta e})/R_{\eta e}$, the dimensionless vibrational coordinate. The coefficient $a_{1\eta}$ in equation (7.171) is the leading anharmonic potential coefficient in Dunham's power series expansion of $V_\eta(R)$ [23]:

$$V_\eta(R) = \left(hc\omega_{\eta e}^2 \big/ 4B_{\eta e}\right)\xi^2(1 + a_{1\eta}\xi + a_{2\eta}\xi^2 + a_{3\eta}\xi^3 + \cdots). \tag{7.173}$$

This form of $V_\eta(R)$ has the advantage of generality and converges well for the lower part of the potential function. It is clear from the form of equation (7.171) that if $X_\eta(R)$ has only a weak dependence on R, the corresponding parameter in the effective Hamiltonian will not depend strongly on the vibrational quantum number either. For example, the isotropic magnetic hyperfine interaction samples the electronic wave

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function in the immediate region around the nucleus. In consequence, it is virtually unaware of the electrons around the other nucleus in a diatomic molecule and consequently the hyperfine parameter is hardly affected by vibrational excitation.

We now turn to the second-order perturbation terms; they are rather numerous since all possible combinations of squared and cross terms can contribute. In practice, we can often be selective and take only those terms which are significant into consideration. For example, the second-order terms produce only minor modifications of the fine structure patterns and are often difficult to separate from the effects of the first-order terms. Probably the most easily observable of the second-order terms are the centrifugal distortion effects associated with the off-diagonal matrix elements of $B_\eta(R)$. There are two reasons for this. First, $B_\eta(R)$ has a fairly strong dependence on r:

$$B_\eta(R) = (\hbar^2/2hc\mu R^2) = \big(\hbar^2/2hc\mu R_{\eta e}^2\big)(1 - 2\xi + 3\xi^2 - 4\xi^3 + \cdots), \quad (7.174)$$

and second, levels with relatively high values of the rotational quantum number N (or J, where appropriate) can often be observed in practice.

Let us first consider the contribution of the rotational kinetic energy,

$$\mathcal{H}_{\rm rot} = B(R)\boldsymbol{N}^2, \quad (7.175)$$

with itself. In second order of perturbation theory, this produces an operator

$$P_0\mathcal{H}'\frac{Q_0}{a}\mathcal{H}'P_0 = \sum_{v'}{}' \sum_{J'} |v;J\rangle \frac{\langle v;J|B(R)\boldsymbol{N}^2|v';J'\rangle\langle v';J'|B(R)\boldsymbol{N}^2|v;J\rangle}{\big[G_v^{(0)} - G_{v'}^{(0)}\big]}\langle v;J|, \quad (7.176)$$

where the restriction to the particular electronic state η is implied. The expression on the right-hand side can be separated into vibrational and rotational factors:

$$P_0\mathcal{H}'\frac{Q_0}{a}\mathcal{H}'P_0 = \left\{\sum_{v'}{}' |v\rangle \frac{\langle v|B(R)|v'\rangle\langle v'|B(R)|v\rangle}{\big[G_v^{(0)} - G_{v'}^{(0)}\big]}\langle v|\right\} \times \left\{\sum_{J'} |J\rangle\langle J|\boldsymbol{N}^2|J'\rangle\langle J'|\boldsymbol{N}^2|J\rangle\langle J|\right\}. \quad (7.177)$$

The rotational factor is further reduced to the matrix element of the operator product $(\boldsymbol{N}^2)(\boldsymbol{N}^2)$ by the closure rule. The contribution can then be expressed in terms of an operator of the form

$$\mathcal{H}_{\rm cd} = -D_{\eta v}(\boldsymbol{N}^2)(\boldsymbol{N}^2) \quad (7.178)$$

which, in the spirit of the effective Hamiltonian, is understood to act only on spin-rotational levels of the vibrational level v in the electronic state $|\eta, \Lambda\rangle$.

The centrifugal distortion constant $D_{\eta v}$ is the result of the second-order vibrational contributions:

$$\begin{aligned} D_{\eta v} &= -\sum_{v'}{}' \frac{\langle \eta, v|B_\eta(R)|\eta, v'\rangle\langle \eta, v'|B_\eta(R)|\eta, v\rangle}{\big[G_{\eta v}^{(0)} - G_{\eta v'}^{(0)}\big]} \\ &= \frac{4B_{\eta e}^3}{\omega_{\eta e}^2} + \left(\frac{6B_{\eta e}^4}{\omega_{\eta e}^3}\right)\big(19 + 18a_{1\eta} + 9a_{1\eta}^2 - 8a_{2\eta}\big)(v + 1/2) + \cdots. \end{aligned} \quad (7.179)$$

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As with the first-order contributions, we see that each parameter in $\mathcal{H}_{\rm eff}$ has a weak vibrational dependence which can in general be modelled as

$$P_v = P_e + \alpha_P(v + 1/2) + \beta_P(v + 1/2)^2 + \cdots. \tag{7.180}$$

Because we have chosen the potential function $V_\eta(R)$ to be independent of the reduced mass in the zeroth-order Hamiltonian, the isotopic dependences of the various terms in (7.179) are quite explicit. The leading term D_{ve} is proportional to μ^{-2} and the vibrational dependent term α_{Dv} is proportional to $\mu^{-5/2}$.

We have seen that the dependence of $B_\eta(R)$ on the vibrational coordinate ξ causes a mixing of the vibrational level of interest with neighbouring levels. This mixing results in centrifugal distortion corrections to all the various parameters $X_\eta(R)$ in the perturbation Hamiltonian $\mathcal{H}'$ when combined in a cross term. The operator has the same form as in the original term, for example, $(2/3)\sqrt{6}\mathrm{T}^2_{q=0}(\boldsymbol{S}, \boldsymbol{S})$ for the spin–spin dipolar term, multiplied by $\boldsymbol{N}^2$. The coefficient which qualifies this term has the general form

$$\begin{aligned} X_{\eta Dv} = \sum_{v'}{}' \{&\langle \eta, v|B_\eta(R)|\eta, v'\rangle\langle \eta, v'|X_\eta(R)|\eta, v\rangle + \langle \eta, v|X_\eta(R)|\eta, v'\rangle \\ &\times \langle \eta, v'|B_\eta(R)|\eta, v\rangle\} \big/ \big[G^{(0)}_{\eta v} - G^{(0)}_{\eta v'}\big]. \end{aligned} \tag{7.181}$$

Following the perturbation treatment of Watson [22], the matrix elements can be evaluated to give

$$\begin{aligned} X_{\eta Dv} = &\big(4B^2_{\eta e}/\omega^2_{\eta e}\big)X'_{\eta e} + \big(2B^3_{\eta e}/\omega^3_{\eta e}\big)\big\{2X'''_{\eta e} - 3\big(1 + 3a_{1\eta}\big)X''_{\eta e} \\ &+ 3\big(8 + 9a_{1\eta} + 9a^2_{1\eta} - 8a_{2\eta}\big)X'_{\eta e}\big\}(v + 1/2) + \cdots. \end{aligned} \tag{7.182}$$

We see from this equation that the centrifugal distortion of interactions which depend only weakly on R will be very small.

7.5.2. The form of the effective Hamiltonian

At this point, it is helpful to collect all the various terms in the zero-field effective Hamiltonian together. We remind ourselves that the effective Hamiltonian is an operator which is confined to act only on the rotational, electron spin and nuclear spin states spanning a given vibrational level of a single electronic state $|\eta, \Lambda\rangle$:

$$\mathcal{H}_{\eta v}/hc = T_{\eta e} + G_{\eta v} + \mathcal{H}_{\rm rot} + \mathcal{H}_{\rm cd} + \mathcal{H}_{\rm so} + \mathcal{H}_{\rm ss} + \mathcal{H}_{\rm sr} + \mathcal{H}_{\Lambda \rm d} + \mathcal{H}_{\rm hfs} + \mathcal{H}_{\rm Q} + \mathcal{H}_{\rm fs}. \tag{7.183}$$

In this expression, $T_{\eta e}$ is the energy origin of the electronic state $|\eta, \Lambda\rangle$ and $G_{\eta v}$ has absorbed the adiabatic and spin contributions to the vibrational potential energy (vibrationally averaged):

$$G_{\eta v} = G^{(0)}_{\eta v} + V^{(\rm ad)}_{\eta v} + V^{(\rm spin)}_{\eta v}. \tag{7.184}$$

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The other contributions are as follows:

rotational kinetic energy

$$\mathcal{H}_{\rm rot} = B_{\eta v}\boldsymbol{N}^2 = \left\{\langle \eta, v|B_\eta(R)|\eta, v\rangle + V_{\eta Dv}^{\rm (ad)} + V_{\eta Dv}^{\rm (spin)}\right\}\boldsymbol{N}^2 \tag{7.185}$$

centrifugal distortion

$$\mathcal{H}_{\rm cd} = -D_{\eta v}(\boldsymbol{N}^2)^2 + H_{\eta v}(\boldsymbol{N}^2)^3 + \cdots \tag{7.186}$$

spin–orbit coupling

$$\mathcal{H}_{\rm so} = (1/2)\left[(A_{\eta v} + A_{\eta Dv}\boldsymbol{N}^2), \mathrm{T}^1_{q=0}(\boldsymbol{L})\mathrm{T}^1_{q=0}(\boldsymbol{S})\right]_+ \tag{7.187}$$

spin–spin coupling

$$\mathcal{H}_{\rm ss} = (\sqrt{6}/3)\left[(\lambda_{\eta v} + \lambda_{\eta Dv}\boldsymbol{N}^2), \mathrm{T}^2_{q=0}(\boldsymbol{S}, \boldsymbol{S})\right]_+ \tag{7.188}$$

spin–rotation interaction

$$\mathcal{H}_{\rm sr} = (1/2)\left[(\gamma_{\eta v} + \gamma_{\eta Dv}\boldsymbol{N}^2), \mathrm{T}^1(\boldsymbol{N})\cdot\mathrm{T}^1(\boldsymbol{S})\right]_+ \tag{7.189}$$

Λ-doubling

$$\begin{aligned}\mathcal{H}_{Ad} = {}& {\sum_{q=\pm1}}' \exp(-2\mathrm{i}q\phi)(1/2)\left\{-\left[(o_{\eta v} + o_{\eta Dv}\boldsymbol{N}^2), \mathrm{T}^2_{2q}(\boldsymbol{S}, \boldsymbol{S})\right]_+\right.\\ &\left. + \left[(p_{\eta v} + p_{\eta Dv}\boldsymbol{N}^2), \mathrm{T}^2_{2q}(\boldsymbol{N}, \boldsymbol{S})\right]_+ - \left[(q_{\eta v} + q_{\eta Dv}\boldsymbol{N}^2), \mathrm{T}^2_{2q}(\boldsymbol{N}, \boldsymbol{N})\right]_+\right\}\end{aligned} \tag{7.190}$$

magnetic hyperfine interactions

$$\begin{aligned}\mathcal{H}_{\rm hfs} = {}& \sum_\alpha \left\{a^\alpha_{\eta v}\mathrm{T}^1_{q=0}(\boldsymbol{I}_\alpha)\mathrm{T}^1_{q=0}(\boldsymbol{L}) + b^\alpha_{\mathrm{F}\eta v}\mathrm{T}^1(\boldsymbol{I}_\alpha)\cdot\mathrm{T}^1(\boldsymbol{S}) + (\sqrt{6}/3)c^\alpha_{\eta v}\mathrm{T}^2_{q=0}(\boldsymbol{I}_\alpha, \boldsymbol{S})\right.\\ &\left. + {\sum_{q=\pm1}}' \exp(-2\mathrm{i}q\phi)d^\alpha_{\eta v}\mathrm{T}^2_{2q}(\boldsymbol{I}_\alpha, \boldsymbol{S})\right\}\end{aligned} \tag{7.191}$$

electric quadrupole interaction

$$\mathcal{H}_{\rm Q} = \sum_\alpha \frac{eQ_\alpha}{4I_\alpha(2I_\alpha - 1)}\left\{\sqrt{6}q^\alpha_0\mathrm{T}^2_{q=0}(\boldsymbol{I}_\alpha, \boldsymbol{I}_\alpha) + {\sum_{q=\pm1}}' \exp(-2\mathrm{i}q\phi)q^\alpha_2\mathrm{T}^2_{2q}(\boldsymbol{I}_\alpha, \boldsymbol{I}_\alpha)\right\} \tag{7.192}$$

higher-order fine structure

$$\begin{aligned}\mathcal{H}_{fs} = {}& C^{(3)}_{\eta v}\mathrm{T}^3(\boldsymbol{L}^2, \boldsymbol{N})\cdot\mathrm{T}^3(\boldsymbol{S}, \boldsymbol{S}, \boldsymbol{S}) + (\sqrt{10}/5)\eta_{\eta v}\mathrm{T}^1_{q=0}(\boldsymbol{L})\mathrm{T}^3_{q=0}(\boldsymbol{S}, \boldsymbol{S}, \boldsymbol{S})\\ &+ (\sqrt{70}/6)\Theta_{\eta v}\mathrm{T}^4_{q=0}(\boldsymbol{S}, \boldsymbol{S}, \boldsymbol{S}, \boldsymbol{S}).\end{aligned} \tag{7.193}$$

In these equations, the square brackets $[,]_+$ indicate anticommutators which are introduced to ensure that the operator is Hermitian. Note that the expression for $B_{\eta v}$ in equation (7.185) is slightly modified from equation (7.171) by the inclusion of the small correction terms $V^{\rm (ad)}_{\eta Dv}$ and $V^{\rm (spin)}_{\eta Dv}$. These centrifugal distortion corrections show up only in the electronic contributions to the isotope effects in $B_{\eta v}$ where they are responsible

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for the adiabatic change in bond length on isotopic substitution. The last contribution to the effective Hamiltonian, in equation (7.193), describes the higher-order fine structure effects. The first of these, a spin–rotation interaction, has already been described in some detail in section 7.4.7. The third term, involving $\Theta_{\eta v}$, is a spin–spin interaction first described by Brown and Milton [20] while the second term, involving $\eta_{\eta v}$, is a higher-order spin–orbit interaction which was introduced by Brown, Milton, Watson, Zare, Albritton, Horani and Rostas [24]. From the arguments presented in section 7.4.7, the $C^{(3)}_{\eta v}$ and $\eta_{\eta v}$ terms only occur in states of quartet or higher multiplicity while the $\Theta_{\eta v}$ term requires the state to be of at least quintet multiplicity. We remind ourselves also that the Λ-doubling terms in equations (7.232), (7.191) and (7.192) are formulated for Π electronic states only.

The parameters in the effective Hamiltonian $\mathcal{H}_{\eta v}$ may not all be determinable from spectroscopic data. When indeterminacies occur, they can often be resolved by utilising data from different isotopic forms. The parameters $X_{\eta v}$ and $X_{\eta D v}$ in the equations above do not themselves have simple isotopic ratios but the coefficients of the powers of $(v + 1/2)$ in the expansions (7.168) and (7.182) do. The isotopic ratios for X_e, X'_e, X''_e, ..., are the same as for $X(R)$ itself and the ratio B_e/ω_e is proportional to $\mu^{-1/2}$. Thus the isotopic ratio for any of the coefficients in $X_{\eta v}$ and $X_{\eta D v}$ is readily determined.

7.5.3. The $\boldsymbol{N}^2$ formulation of the effective Hamiltonian

We have been careful in our formulation of the effective Hamiltonian to represent the square of the rotational angular momentum by the operator $\boldsymbol{N}^2$, as in equation (7.185), for example. There are many papers in the literature, however, where the authors use the operator $\boldsymbol{R}^2 = (\boldsymbol{N} - \boldsymbol{L})^2$ instead. Their justification for doing this is that the expression for the rotational kinetic energy in the full Hamiltonian is

$$\mathcal{H}_{\text{rot}} = B(R)\boldsymbol{R}^2 \tag{7.194}$$

and so this operator might be expected to give a more faithful representation of the rotational motion. The difficulty with the $\boldsymbol{R}^2$ operator is that, as we have seen in section 7.4.2, it involves the orbital angular momentum operator $\boldsymbol{L}$ which in turn has matrix elements which are off-diagonal in the electronic state as well as diagonal. In section 7.4.2, we worked through the implications of this mixing to show that the *effective* rotational Hamiltonian for a given electronic state has the form

$$\mathcal{H}_{\text{rot}}(\textit{eff}) = B_\eta(R)\boldsymbol{N}^2 \tag{7.195}$$

where the effects of the off-diagonal elements have been absorbed into the parameter $B_\eta(R)$. The same remarks apply to all second-order terms in the effective Hamiltonian which involve the mixing of electronic states through the rotational kinetic energy operator, such as the spin–rotation interaction or Λ-doubling. For all of these operators in the effective Hamiltonian the rotational angular momentum is represented by $\boldsymbol{N}$ rather than $\boldsymbol{R}$. Therefore if the effective Hamiltonian is developed in the way described in this

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Table 7.2. *The interconversion of parameters in the N^2 and R^2 Hamiltonians. The symbol X represents any molecular parameter other than G, B or D*

$G_{\eta v}(N^2) = G_{\eta v}(R^2) - \Lambda^2 B_{\eta v}(R^2) - \Lambda^4 D_{\eta v}(R^2) - \Lambda^6 H_{\eta v}(R^2) - \cdots$
$B_{\eta v}(N^2) = B_{\eta v}(R^2) + 2\Lambda^2 D_{\eta v}(R^2) + 3\Lambda^4 H_{\eta v}(R^2) + \cdots$
$D_{\eta v}(N^2) = D_{\eta v}(R^2) + 3\Lambda^2 H_{\eta v}(R^2) + \cdots$
$X_{\eta v}(N^2) = X_{\eta v}(R^2) - \Lambda^2 X_{\eta v D}(R^2) + \Lambda^4 X_{\eta v H}(R^2) + \cdots$
$X_{\eta v D}(N^2) = X_{\eta v D}(R^2) - 2\Lambda^2 X_{\eta v H}(R^2) + \cdots$
$X_{\eta v H}(N^2) = X_{\eta v H}(R^2) + \cdots$

book, there are strong grounds for using the N^2 formulation. The use of R^2 is not justified and indeed causes some difficulties in practice. Those parts of its matrix elements which depend on $\boldsymbol{L}$ or $\boldsymbol{L}^2$ are not well defined because the diatomic molecule wave functions are not eigenfunctions of $\boldsymbol{L}^2$; the quantity $\langle \eta, \Lambda | \boldsymbol{L}^2 | \eta, \Lambda \rangle$ must be evaluated by *ab initio* methods. Workers who claim to be using the R^2 formulation get round this difficulty by dropping the $\boldsymbol{L}^2$ term altogether, which can be very deceptive. Another tricky aspect of using R^2 for the formulation of centrifugal distortion terms is that

$$\langle J | \boldsymbol{R}^4 | J \rangle \neq \{\langle J | \boldsymbol{R}^2 | J \rangle\}^2. \tag{7.196}$$

Failure to recognise this leads to the introduction of extra terms in the Hamiltonian. To summarise, a Hamiltonian formulated in terms of N^2 has the highly desirable characteristic that each term is the product of a determinable parameter which governs the magnitude of the interaction and an angular momentum operator whose matrix elements are fully defined. The difficulties associated with the effect of the $\boldsymbol{L}^2$ terms are confined to the interpretation of parameters in the effective Hamiltonian and their comparison with *ab initio* calculations.

When comparing one's results with those of other workers, it is important to check the detailed form of the Hamiltonian which has been used. If it is an R^2 Hamiltonian, the parameters will have different definitions from those in the N^2 Hamiltonian and so will have different values. The relationship between the two sets of parameters is easy to work out provided that the R^2 formulation has suppressed the off-diagonal matrix elements of $\boldsymbol{L}$ in the manner described above, that is, $\boldsymbol{R}$ is defined as

$$\boldsymbol{R} = N_x \boldsymbol{i} + N_y \boldsymbol{j} + (N_z - L_z)\boldsymbol{k}. \tag{7.197}$$

The relationships between the two sets of parameters for an electronic state $|\eta, \Lambda\rangle$ are given in table 7.2.

7.5.4. The isotopic dependence of parameters in the effective Hamiltonian

To a good approximation, all the parameters in the effective Hamiltonian presented in section 7.5.2 have a well-defined and easily constructed dependence on the reduced

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mass μ of the diatomic molecule. However, as we have seen in the case of the rotational constant B_v in equation (7.85), there are some higher-order corrections which tend to spoil the simple isotopic dependence. In the particular case of B_v, these corrections arise from non-adiabatic mixing of different electronic states, but there are also higher-order terms arising in the vibrational averaging process which have a similar effect. This more detailed isotopic dependence has been investigated by several authors [25, 26] culminating in a definitive paper by Watson [27].

Watson's treatment applies to vibration–rotation effects in diatomic molecules in singlet electronic states; it has not yet been extended to include spin–dependent phenomena. It is based on the Dunham expansion [23] which we met earlier in the previous chapter,

$$E(v, J) = hc \sum_{k\ell} Y_{k\ell}(v + 1/2)^k [J(J + 1) - \Lambda^2]^\ell, \tag{7.198}$$

where v and J are, as usual, the vibrational and rotational quantum numbers. Values for the Dunham coefficients $Y_{k\ell}$ can be determined from experimental data; the point at which the expansion in equation (7.198) is truncated depends on the range of v and J values available and on the precision of the data. For different isotopic forms of the same molecule, which have essentially the same potential energy function $V_\eta(R)$ in equation (7.169), the $Y_{k\ell}$ are related approximately by

$$Y_{k\ell} \cong \mu^{-(k+2\ell)/2} U_{k\ell}, \tag{7.199}$$

where $U_{k\ell}$ is isotopically invariant. This corresponds to the level of treatment in the previous section. It is, however, not adequate for the most accurate of modern measurements which require corrections to be added to equation (7.199).

These corrections are of two types. The first arises from quantum effects in the calculation of vibration–rotation energy levels and was originally discussed by Dunham himself [23]. He used semiclassical methods, discussed in section 6.13.2, to derive his results. Use of the first-order quantisation condition

$$(2\mu)^{1/2} \int \left[E_\eta^0(v, J) - V_{\eta J}(R)\right]^{1/2} \mathrm{d}R = h(v + 1/2) \tag{7.200}$$

gives the familiar formula in equation (7.198) with the isotopic dependence described in equation (7.199). The corrections to this result arise from the use of the second-order quantisation condition,

$$\begin{aligned}(2\mu)^{1/2} \int \left[E_\eta^0(v, J) - V_{\eta J}(R)\right]^{1/2} \mathrm{d}R - \left\{\hbar^2/32(2\mu)^{1/2}\right\} \\ \times \int \{V'_{\eta J}(R)\}^2 \left[E_\eta^0(v, J) - V_{\eta J}(R)\right]^{-5/2} \mathrm{d}R = h(v + 1/2),\end{aligned} \tag{7.201}$$

where

$$V'_{\eta J}(R) = \frac{\mathrm{d}V_{\eta J}(R)}{\mathrm{d}R}. \tag{7.202}$$

Specifically, the corrections arise from the second-order integral in this condition. The same result can, of course, be derived in a purely quantum calculation using perturbation

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theory. We shall not go into details but the way in which these higher-order corrections arise can be appreciated from the following discussion.

The anharmonic corrections to the vibrational energy levels can be derived from the solutions of the Schrödinger equation with a potential of the form

$$V(q) = (1/2)kq^2 + gq^3 + hq^4 + \cdots \tag{7.203}$$

as discussed in section 6.8.3; in this equation, the vibrational coordinate q is equal to $(R_e - R)$. The effects of the anharmonic terms in this potential can be treated by perturbation theory using the harmonic oscillator eigenfunctions $|v\rangle$ as the zeroth-order basis set. The non-zero matrix elements in this treatment are of the form

$$\langle v+1|q|v\rangle = A(v+1/2)^{1/2} \tag{7.204}$$

where

$$A = (\hbar/4\pi\mu\nu)^{1/2}. \tag{7.205}$$

The quartic term hq^4 makes a contribution in first order of perturbation theory of the form

$$\begin{aligned}\langle v|hq^4|v\rangle &= hA^4\{(2v+1)^2 + 2v^2 + 2v + 2\} \\ &= hA^4\{6(v+1/2)^2 + 3/2\}.\end{aligned} \tag{7.206}$$

Use of equation (7.205) shows that A^4 is proportional to μ^{-1}. We thus see that there is a contribution $6hA^4$ to the Dunham coefficient Y_{20} (or $\omega_e x_e$) since it is the coefficient of $(v+1/2)^2$ in the expansion (7.198); this term has the expected reduced mass dependence. However, there is also a small contribution $3hA^4/2$ to the coefficient Y_{00} with the wrong reduced mass dependence (μ^{-1}). This is an example of the higher-order corrections revealed by Dunham's calculation.

The other way in which these corrections can arise is from non-adiabatic correction terms, that is, through the breakdown of the Born–Oppenheimer separation. They were first identified by Van Vleck [28]. We have seen how these contributions can be given explicit form in the derivation of the effective electronic Hamiltonian described in section 7.4. Some of the reduced mass dependencies are easy to track because they enter explicitly into the calculation as shown, for example, in the derivation of the second order contribution $B^{(2)}$ to the rotational constant in section 7.4.2. Other effects are more subtle. For example, one might naively believe that the electron orbital angular momentum $\boldsymbol{L}$ is independent of isotopic substitution. However, this is not so because the angular momentum is measured relative to the *nuclear* centre of mass in our formulation. Since the geometrical position of the nuclear centre of mass changes on isotopic substitution, so too does the orbital angular momentum. The details are all laid out clearly in Watson's paper [27]. Generally speaking, the Dunham corrections are rather small compared with those from the Born–Oppenheimer breakdown.

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Collecting all these various contributions together, Watson showed that a more accurate description of the isotopic mass dependence is given by

$$Y_{k\ell} = \mu_C^{-(k+2\ell)/2} U_{k\ell} \left\{ 1 + \frac{m_e}{M_1} \Delta_{k\ell}^{(1)} + \frac{m_e}{M_2} \Delta_{k\ell}^{(2)} + O\left(\frac{m_e^2}{M_i^2} \right) \right\}, \tag{7.207}$$

where m_e is the electron mass, M_1 and M_2 are here the *atomic* masses of atoms 1 and 2, and μ_C is a charge-modified reduced mass defined by

$$\mu_C = \frac{M_1 M_2}{(M_1 + M_2 - C m_e)} \tag{7.208}$$

in which C is the charge number of the molecule. The denominator of μ_C is thus the total mass of the molecule or ion; for a neutral species it is the reduced atomic mass (because to a good approximation the electrons follow the nuclear motion closely). The dimensionless quantities $\Delta_{k\ell}^{(i)} (i = 1, 2)$ are isotopically invariant and are expected to be of the order unity for a well isolated electronic state. The even higher order corrections $O(m_e/M_i)^2$ in equation (7.207) are usually too small to be characterised experimentally.

The $U_{k\ell}$ are isotopically invariant parameters. Our discussion of the RKR potential in section 6.13.3 showed that the potential $V_\eta(R)$ can be determined from a knowledge of G_v and B_v. Since the parameters $U_{k\ell}$ with $\ell \geq 2$ can be calculated from $V_\eta(R)$, it follows that they are exactly determined by the values of $U_{k\ell}$ with $\ell = 0$ and 1. The simplest case of U_{02} is a familiar one. The relationship in question,

$$Y_{02} \simeq -4 Y_{01}^3 \big/ Y_{01}^2, \tag{7.209}$$

more usually written as

$$D_e \simeq 4 B_e^3 \big/ \omega_e^2, \tag{7.210}$$

is not exact because the correction terms on each side do not balance (see equation (7.179)). However the corresponding relationship between the $U_{k\ell}$ parameters,

$$U_{02} = -4 U_{01}^3 \big/ U_{01}^2, \tag{7.211}$$

is exact because the correction terms have been removed. This and similar relationships provide convenient constraints when fitting data.

7.6. Effective Zeeman Hamiltonian

Many informative experiments can be carried out on diatomic molecules in the presence of an external magnetic field, irrespective of whether they are in closed or open shell states. An external magnetic field destroys the isotropy of free space, as a consequence of which the degeneracy of the different orientations of the molecule is lifted. In other words, the states of different orientation have different energies in the magnetic field. These splittings are observable and provide a measurement of the magnetic dipole moment of the molecule in the particular spin–rotational level involved. The magnetic

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moment depends on the electronic structure of the molecule; measurement of this quantity therefore provides information about the structure.

The effect of a magnetic field on a diatomic molecule has been described in detail in section 3.7. An extra term is added to the magnetic vector potential of each electron i of the form

$$\boldsymbol{A}_i^B = (1/2)(\boldsymbol{B} \wedge \boldsymbol{R}_i) \tag{7.212}$$

where $\boldsymbol{B}$ is the uniform applied flux density. When this additional contribution is substituted into the electronic Hamiltonian and the coordinates are transformed to the molecule-fixed axis system, the various Zeeman terms given in chapter 3 are obtained. There are several of them, with the largest arising from the interactions with the magnetic moments produced by the orbital and spin motion of the electron. Most of the terms are linear in $\boldsymbol{B}$ and represent the interaction of the flux density with the magnetic dipole moment of the molecule:

$$\mathcal{H}_Z = -\boldsymbol{\mu_m} \cdot \boldsymbol{B}. \tag{7.213}$$

There are also some smaller terms which are quadratic in $\boldsymbol{B}$ and have the general form

$$\mathcal{H}_{\text{susc}} = -\boldsymbol{B} \cdot \boldsymbol{\chi} \cdot \boldsymbol{B}, \tag{7.214}$$

where $\boldsymbol{\chi}$ is the magnetic susceptibility tensor. It is more convenient to express this interaction using spherical tensor notation [29]:

$$\mathcal{H}_{\text{susc}} = -\frac{1}{2} {\sum_{k=0,2}}' \mathrm{T}^k(\boldsymbol{\chi}) \cdot \mathrm{T}^k(\boldsymbol{B}, \boldsymbol{B}). \tag{7.215}$$

The scalar contribution, with $k = 0$, is constant for all levels of a molecule and so cannot be measured in practice. The anisotropic $k = 2$ contribution, on the other hand, is readily determinable.

We see that there are many contributions to the Zeeman Hamiltonian, all of which must be taken into account in the construction of the effective Hamiltonian. In order to focus our attention, let us consider just one of the dipolar terms, namely, the interaction involving the orbital motion of the electrons:

$$\mathcal{H}'_Z = \frac{e}{2m} \sum_i \boldsymbol{B} \cdot \left\{ \boldsymbol{r}_i - \frac{m}{M} \sum_j \boldsymbol{r}_j \right\} \wedge \boldsymbol{p}_i. \tag{7.216}$$

We can write this more simply as

$$\mathcal{H}'_Z = g_L \mu_B \boldsymbol{B} \cdot \boldsymbol{L}, \tag{7.217}$$

where $\mu_B = e\hbar/2m$ is the Bohr magneton and $\hbar \boldsymbol{L}$ is the orbital angular momentum of the electrons measured relative to the origin of the molecule-fixed axis system (x, y, z). The parameter g_L is the orbital g-factor. Since it has a value of 1.0, one might query the need for its introduction. We shall see later that the value will deviate from unity when it is absorbed into the effective Hamiltonian. The direction of the uniform flux density $\boldsymbol{B}$ in equation (7.217) serves to define the orientation of the laboratory-fixed coordinate system. By convention, $\boldsymbol{B}$ is taken to point along the Z

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axis so that B_X and B_Y are zero. The interaction therefore involves L_Z which can be written in terms of the molecule-fixed components by use of the direction cosines,

$$L_Z = -\sin\theta\cos\chi L_x + \sin\theta\sin\chi L_y + \cos\theta L_z, \tag{7.218}$$

or in spherical tensor notation by the use of rotation matrices

$$\mathrm{T}^1_{p=0}(\boldsymbol{L}) = \sum_q \mathfrak{D}^{(1)}_{0q}(\omega)^* \mathrm{T}^1_q(\boldsymbol{L}). \tag{7.219}$$

Here, ω represents the Euler angles (ϕ, θ, χ). Thus when we come to work out the effects of the orbital Zeeman interaction, we see that it has off-diagonal matrix elements which link electronic states with $\Delta\Lambda = 0, \pm 1$, as well as purely diagonal elements. It is clearly desirable to remove the effect of these matrix elements by a suitable perturbative transformation to achieve an effective Zeeman Hamiltonian which acts only within the spin–rotational levels of a given electronic state $|\eta, \Lambda, v\rangle$, in the same way as the zero-field effective Hamiltonian in equation (7.183).

In order to appreciate how the effective Zeeman Hamiltonian is derived, let us consider the mixing effects of the orbital magnetic interaction $\mathcal{H}'_Z$ in equation (7.217) along with the rotational Hamiltonian $\mathcal{H}_{\mathrm{rot}}$, equation (7.80), and the spin–orbit coupling term $\mathcal{H}_{\mathrm{so}}$ in equation (7.72). These are absorbed into the effective Hamiltonian in a procedure which will by now be quite familiar and involves degenerate perturbation theory. The first-order contribution of $\mathcal{H}'_Z$ simply introduces this leading term into the Zeeman Hamiltonian. The second-order contributions involve both squared and cross terms. It can be seen that the cross term of $\mathcal{H}'_Z$ with $\mathcal{H}_{\mathrm{rot}}$ or $\mathcal{H}_{\mathrm{so}}$ produces a term which is linear in the magnetic flux density $\boldsymbol{B}$ and will therefore have the same form as the first order contribution. The cross term between $\mathcal{H}'_Z$ and $\mathcal{H}_{\mathrm{so}}$ gives an operator of the following form:

$$P_0\mathcal{H}'\frac{Q_0}{a}\mathcal{H}'P_0 = P_0\left\{\left[\sum_{q=\pm1}{}'\sum_{\eta'\Lambda'}\sum_{S'\Sigma'}\sum_{J'\Omega'M'}\frac{ME_1\times ME_2 + transpose}{V_\eta(R) - V_{\eta'}(R)}\right]\right\}P_0 B_Z, \tag{7.220}$$

where

$$ME_1 = \langle \eta, \Lambda; S, \Sigma; J, \Omega, M|(-1)^q A\mathrm{T}^1_q(\boldsymbol{L})\mathrm{T}^1_{-q}(\boldsymbol{S})|\eta', \Lambda'; S', \Sigma'; J', \Omega', M'\rangle,$$
$$ME_2 = \langle \eta', \Lambda'; S', \Sigma'; J', \Omega', M'|g_L\mu_B\mathfrak{D}^{(1)}_{0,-q}(\omega)^*\mathrm{T}^1_{-q}(\boldsymbol{L})|\eta, \Lambda; S, \Sigma; J, \Omega, M\rangle.$$

This expression can be factorised into orbital, spin and rotational parts and then tidied up to produce an effective operator of the form

$$g_l\mu_B B_Z \sum_{q=\pm1}{}'\mathfrak{D}^{(1)}_{0q}(\omega)^*\mathrm{T}^1_q(\boldsymbol{S}). \tag{7.221}$$

The dimensionless parameter g_l is defined by

$$g_l = -g_L\sum_{q=\pm1}{}'\sum_{\eta'\Lambda'}(V_{\eta\Lambda}(R) - V_{\eta'\Lambda'}(R))^{-1}\langle \eta, \Lambda|A\mathrm{T}^1_q(\boldsymbol{L})|\eta', \Lambda'\rangle$$
$$\times\langle \eta', \Lambda'|\mathrm{T}^1_{-q}(\boldsymbol{L})|\eta, \Lambda\rangle. \tag{7.222}$$

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The restricted summation in equation (7.221) means that, for this contribution, the Zeeman energy depends on the x and y components of $\boldsymbol{S}$ only (i.e. it has cylindrical symmetry). It is therefore referred to as the anisotropic correction to the electron spin Zeeman term, which has the isotropic form $g_S \mu_B \boldsymbol{B} \cdot \boldsymbol{S}$.

The cross term between $\mathcal{H}'_Z$ and $\mathcal{H}_{\rm rot}$ can be treated in exactly the same way. The result is a second-order contribution to the effective Zeeman Hamiltonian of the form

$$g_r^e \mu_B B_Z \mathrm{T}^1_{p=0}(\boldsymbol{N}) \tag{7.223}$$

where

$$g_r^e = 2g_L \sum_{q=\pm 1}{}' \sum_{\eta' \Lambda'} (V_{\eta\Lambda}(R) - V_{\eta'\Lambda'}(R))^{-1} \langle \eta, \Lambda | \mathrm{T}^1_q(\boldsymbol{L}) | \eta', \Lambda' \rangle \times \langle \eta', \Lambda' | B(R) \mathrm{T}^1_{-q}(\boldsymbol{L}) | \eta, \Lambda \rangle. \tag{7.224}$$

This term describes the electronic contribution to the rotational g-factor. The contribution (7.223) represents the interaction between the applied magnetic field B_Z and the magnetic moment produced by the electrons in the molecule as it rotates in laboratory space. It has an operator form identical to that of the first-order nuclear orbital (i.e. rotational) Zeeman interaction

$$-g_r^N \mu_B B_Z \mathrm{T}^1_{p=0}(\boldsymbol{N}) \tag{7.225}$$

where

$$g_r^N = \frac{m\left(Z_1 M_2^2 + Z_2 M_1^2\right)}{M_1 M_2 \left(M_1 + M_2\right)}. \tag{7.226}$$

These terms are usually combined into a single operator which describes the magnetic interaction between the external field and the rotation of the molecule as a whole, both electrons and nuclei,

$$\mathcal{H}_{\rm Z,rot} = -g_r \mu_B B_Z \mathrm{T}^1_{p=0}(\boldsymbol{N}), \tag{7.227}$$

with

$$g_r = g_r^N - g_r^e. \tag{7.228}$$

In rotational motion the electrons tend to follow the nuclei quite closely because of the strong Coulombic interaction. As a consequence, there is a fair degree of cancellation implied by equation (7.228).

The second-order contribution of the orbital Zeeman term $\mathcal{H}'_Z$ with itself produces a term in the effective Hamiltonian which is quadratic in $\boldsymbol{B}$. It therefore has the same form as the diamagnetic susceptibility contribution to the energy; it provides the paramagnetic or 'high-frequency' contribution to the susceptibility of the molecular system. The resultant term in the effective Zeeman Hamiltonian is

$$\mathcal{H}_{\rm Z,susc} = \mathfrak{L} \mathrm{T}^2_{q=0}(\boldsymbol{B}, \boldsymbol{B}). \tag{7.229}$$

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The parameter $\mathfrak{L}$ is the sum of first- and second-order contributions, $\mathfrak{L}^{(1)}$ and $\mathfrak{L}^{(2)}$, where

$$\mathfrak{L}^{(1)} = -(e^2/8m)\sum_i \langle \eta, \Lambda|\mathrm{T}^2_0(\boldsymbol{r}_i, \boldsymbol{r}_i)|\eta, \Lambda\rangle \tag{7.230}$$

and

$$\mathfrak{L}^{(2)} = g_L^2\mu_B^2(5)^{1/2}\sum_{\eta'\Lambda' q}(V_{\eta\Lambda}(R) - V_{\eta'\Lambda'}(R))^{-1}(-1)^q \begin{pmatrix} 1 & 2 & 1 \\ -q & 0 & q \end{pmatrix} \times \left|\langle \eta, \Lambda|\mathrm{T}^1_q(\boldsymbol{L})|\eta', \Lambda'\rangle\right|^2. \tag{7.231}$$

The form of the complete Zeeman effective Hamiltonian for a diatomic molecule in a given vibrational level of an open shell state has been given by Brown, Kaise, Kerr and Milton [30]. It is the sum of the following terms:

electron spin (*parameter* g_S)

$$g_S\mu_B B_Z \mathrm{T}^1_{p=0}(\boldsymbol{S})$$

electron orbital motion (*parameter* g'_L, *corrected for relativistic, diamagnetic* [29] *and non-adiabatic* [31] *effects*)

$$g'_L\mu_B B_Z \mathrm{T}^1_{p=0}(\boldsymbol{L})$$

rotational motion (*parameter* g_r)

$$-g_r\mu_B B_Z \mathrm{T}^1_{p=0}(\boldsymbol{N})$$

anisotropic correction to the electron spin interaction (*parameter* g_l)

$$g_l\mu_B B_Z {\sum_{q=\pm1}}' \mathfrak{D}^{(1)}_{0q}(\omega)^* \mathrm{T}^1_q(\boldsymbol{S})$$

nuclear spin interaction (*parameter* g_N^α, *where* α *labels the nuclei*)

$$-\sum_\alpha g_N^\alpha \mu_N B_Z \mathrm{T}^1_{p=0}(\boldsymbol{I}^\alpha)$$

anisotropic susceptibility (*parameter* $\mathfrak{L}$)

$$\mathfrak{L}\mathrm{T}^2_{q=0}(\boldsymbol{B}, \boldsymbol{B})$$

parity-dependent contributions for a Π *state* (*parameters* g'_l *and* g'^e_r)

$$\mu_B B_Z {\sum_{q=\pm1}}' \exp(-2\mathrm{i}q\phi)\Big\{g'_l \mathfrak{D}^{(1)}_{0,-q}(\omega)^* \mathrm{T}^1_q(\boldsymbol{S}) - g_r^{e'}\sum_p (-1)^p \mathfrak{D}^{(1)}_{-p,-q}(\omega)^* \mathrm{T}^1_p(\boldsymbol{N}) \mathfrak{D}^{(1)}_{0,-q}(\omega)^*\Big\}. \tag{7.232}$$

It should be appreciated that the Zeeman interactions are usually dominated by the first two terms in (7.232), the electron spin and orbital terms. The other terms are typically between two and four orders of magnitude smaller. For a molecule in a closed shell $^1\Sigma$ state, only the rotational Zeeman term, the nuclear spin contribution and the susceptibility term survive.

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A recent paper [32] has suggested that the primary g-factors, g_S and g'_L, should be defined as *negative* quantities so that they reveal the alignment of the magnetic dipole moment relative to the angular momentum. If this convention is adopted, the signs of the two contributions to the effective Zeeman Hamiltonian, given above, must be reversed.

7.7. Indeterminacies: rotational contact transformations

If the values of the parameters for the vibronic state $|\eta, v\rangle$ are known *a priori*, the spin–rotational energy levels can be calculated in a straightforward manner from the effective Hamiltonian, equation (7.183), by computing the matrix elements in a suitable basis set and diagonalising the sub-matrices numerically for each value of the quantum number J (or F if hyperfine effects are included). In practice, however, $\mathcal{H}_{\eta v}$ is usually used as an empirical Hamiltonian with parameters to be determined by optimisation of the agreement between computed and observed spectra. In this inversion procedure, the possibility of indeterminacy arises, because different terms in equation (7.183) can make indistinguishable contributions to the eigenvalues, in much the same way as $B^{(1)}(R)$ and $B^{(2)}(R)$, for example, make indistinguishable contributions to the effective rotational Hamiltonian, equation (7.86). These are theoretical indeterminacies, caused by the non-uniqueness of the solution of these equations, rather than experimental indeterminacies due to shortage of data. The latter type of indeterminacy may also be present, of course, and often is.

The solution to this problem which is usually adopted in practice is to constrain particular parameters to preset values, usually zero, in a least-squares fit of the Hamiltonian to the data. This has the effect of modifying the values obtained for the other parameters in the Hamiltonian. In order to interpret the results in this situation, it is necessary to subject the effective Hamiltonian $\mathcal{H}_{\eta v}$ to yet another transformation to bring it into the form which is actually used in the empirical fit. Before we do this, however, let us consider a particular example to help us understand the nature of these indeterminacies. There is a well-known indeterminacy between the parameters $\gamma_{\eta v}$ and $A_{\eta D v}$ in the Hamiltonian for a molecule in a $^2\Pi$ state, first pointed out by Veseth [33]. If we confine ourselves to the simple Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\rm so} + \mathcal{H}_{\rm rot} + \mathcal{H}_{\rm sr} \tag{7.233}$$

where the three terms are given by equations (7.187), (7.185) and (7.189), the representation for a given J value is the following 2×2 matrix.

	$\lvert J, 3/2\rangle$	$\lvert J, 1/2\rangle$
$\lvert J, 3/2\rangle$	$(1/2)\{A + A_D z\} + Bz$	$-(B - \gamma/2)\sqrt{z}$
$\lvert J, 1/2\rangle$	$-(B - \gamma/2)\sqrt{z}$	$-(1/2)\{A + A_D(z+2)\} + B(z+2) - \gamma$

In this matrix

$$z = (J - 1/2)(J + 3/2) = (J + 1/2)^2 - 1. \tag{7.234}$$

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The eigenvalues of the matrix are

$$E_{\pm} = B(z+1) - \gamma/2 - A_D/2 \pm (1/2)[\{(A - 2B + \gamma) + A_D(z+1)\}^2 + 4(B - \gamma/2)^2 z]^{1/2} \tag{7.235}$$

The terms inside the square root part of this expression may be rearranged in increasing powers of z, to give

$$[\ ]^{1/2} = \left[\{(A - 2B + \gamma) + A_D\}^2 + \{2A_D(A - 2B + \gamma) + 4(B - \gamma/2)^2\}z + A_D^2 z^2\right]^{1/2}. \tag{7.236}$$

If we make measurements of the energy levels for different J values, the coefficients of the different powers of z are determinable. Thus the following combinations can be determined:

$$(1/2)(\mathcal{H}_{11} + \mathcal{H}_{22}) = B(z+1) - \gamma/2 - A_D/2, \tag{7.237}$$

and, inside the square root,

$$\text{coefficient of } z^0 = \{A - 2B + \gamma + A_D\}^2, \tag{7.238}$$

$$\text{coefficient of } z^1 = \{2A_D(A - 2B + \gamma) + 4(B - \gamma/2)^2\}, \tag{7.239}$$

$$\text{coefficient of } z^2 = A_D^2. \tag{7.240}$$

The combination in equation (7.237) allows the value for B to be determined from the z dependence. With this value, it is possible to determine $(A + \gamma + A_D)$ from equation (7.238). Since it is preferable to produce definite values for the major parameters, let us say that this coefficient gives a value for A. The coefficient of z^1, in equation (7.239), on the other hand, gives us a linear combination of A_D and γ; this is the equation which defines the nature of the indeterminacy between A_D and γ. If the coefficient of z^2 in equation (7.240) can be determined (it is very small in practice), it would appear that γ and A_D can be separated. In other words, the values of all four parameters in the Hamiltonian can be obtained. However, at this level of approximation, we have also to include the next two terms in the centrifugal expansion of $\mathcal{H}_{so}$ and $\mathcal{H}_{sr}$ (A_H and γ_D) which contribute to the coefficient of z^2 as well. Thus only three of the four parameters in equation (7.235) can be determined. We choose these to be B, A and the coefficient of z^1 in equation (7.239). In practice, we might choose to constrain γ to zero in the fit and then determine an effective value for A_D, denoted by $\tilde{A}_D$. Substitution in equation (7.239) gives

$$\begin{aligned}\{2\tilde{A}_D(A - 2B) + 4B^2\} &= \{2A_D(A - 2B + \gamma) + 4(B - \gamma/2)^2\} \\ &\simeq 2A_D(A - 2B) + 4B^2 - 4B\gamma,\end{aligned} \tag{7.241}$$

provided the magnitude of γ is much smaller than B. Hence we see that the effective parameter is related to the true value for A_D and γ by

$$\tilde{A}_D = A_D - 2B\gamma/(A - 2B). \tag{7.242}$$

Conversely, if we choose to constrain A_D to zero, we determine a value for the effective

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spin–rotation parameter $\tilde{\gamma}$ where

$$\tilde{\gamma} = \gamma - (A - 2B)A_D/2B. \tag{7.243}$$

Brown and Watson [17] have shown that it is possible to break the indeterminacy implicit in equation (7.239) by combining data for different isotopic forms. This separation makes use of the fact that all three parameters on the right-hand side of equation (7.242) are, to a good approximation, proportional to μ^{-1} where μ is the reduced mass of the diatomic molecule. Thus the first term on the right-hand side is proportional to μ^{-1} while the second is proportional to μ^{-2}. This allows the true values for γ and A_D to be determined. Similar arguments apply to equation (7.243). The resolution of this method depends directly on the fractional change in μ on isotopic substitution.

Brown, Colbourn, Watson and Wayne [7] have shown that this type of indeterminacy occurs for any ${}^{2S+1}\Lambda$ state which conforms to Hund's case (a) coupling. This result can be established most easily by applying a contact transformation to the effective Hamiltonian. Let us divide $\mathcal{H}_{\eta v}$ into a principal part $\mathcal{H}^{(0)}_{\eta v}$ and a remainder $\mathcal{H}^{(1)}_{\eta v}$:

$$\mathcal{H}_{\eta v} = \mathcal{H}^{(0)}_{\eta v} + \mathcal{H}^{(1)}_{\eta v} \tag{7.244}$$

with

$$\mathcal{H}^{(0)}_{\eta v} = T_{\eta e} + G_{\eta v} + B_{\eta v}\boldsymbol{N}^2 + A_{\eta v}L_z S_z + (2/3)\lambda_{\eta v}\big(3S_z^2 - \boldsymbol{S}^2\big). \tag{7.245}$$

Following the procedure described in section 7.3, we apply a similarity transformation to the Hamiltonian to produce a transformed Hamiltonian,

$$\tilde{\mathcal{H}}_{\eta v} = \mathrm{e}^{\mathrm{i}F}\mathcal{H}_{\eta v}\mathrm{e}^{-\mathrm{i}F}, \tag{7.246}$$

where F is the transformation operator for a particular vibronic state $|\eta, v\rangle$. Following equations (7.53), (7.54) and (7.55), we expand the exponential operators to give

$$\tilde{\mathcal{H}}_{\eta v} = \mathcal{H}^{(0)}_{\eta v} + \big\{\mathcal{H}^{(1)}_{\eta v} + \mathrm{i}\big[F, \mathcal{H}^{(0)}_{\eta v}\big]\big\} + \big\{\mathrm{i}\big[F, \mathcal{H}^{(1)}_{\eta v}\big] - (1/2)\big[F, \big[F, \mathcal{H}^{(0)}_{\eta v}\big]\big]\big\} + \cdots. \tag{7.247}$$

Here, terms within the same set of braces are assumed to have the same order of magnitude. As long as F is chosen to be small, the expansion in equation (7.247) will converge rapidly and can be truncated after the first set of braces. Apart from this truncation, the eigenvalues of $\tilde{\mathcal{H}}_{\eta v}$ and $\mathcal{H}_{\eta v}$ are equal. The operator F is chosen suitably to remove terms in $\mathcal{H}^{(1)}_{\eta v}$ and so to eliminate redundancies. At the same time, the coefficients of other terms in $\mathcal{H}^{(1)}_{\eta v}$ may be modified. It is these modified parameters whose values are determined empirically.

The operator F must be taken to be Hermitian (to ensure that the transformation (7.246) is unitary), totally symmetric and of odd degree in the angular momenta. The last requirement follows from the fact that the non-vanishing commutation relationships between angular momentum components, say J_α, reduce the power of the operators by one. The result of the transformation is therefore of even power in $\boldsymbol{J}$ which is required if the term in $\tilde{\mathcal{H}}_{\eta v}$ is to be symmetric with respect to time reversal. To illustrate the procedure, let us consider the operator chosen by Brown and Watson [17]:

$$F_1 = s_1(\boldsymbol{J} \wedge \boldsymbol{S})_z L_z = s_1(J_x S_y - J_y S_x)L_z. \tag{7.248}$$

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When this operator is substituted into equation (7.246), it corresponds to a small rotation in rotational–spin–orbital space. The parameter s_1 governs the magnitude of this rotation. It is a variable parameter which can be chosen to eliminate terms from the transformed Hamiltonian. Using this form for F_1 and the well known commutation relations between the molecule-fixed components of $\boldsymbol{J}$, $\boldsymbol{S}$ and $\boldsymbol{L}$, it is easy to show that

$$\begin{aligned}\mathrm{i}\big[F_1, H_{\eta v}^{(0)}\big] = s_1\{&-A_{\eta v}\Lambda^2\boldsymbol{S}^2 + (A_{\eta v}\Lambda^2 - 4\lambda_{\eta v}\boldsymbol{S}^2)L_zS_z + (A_{\eta v} + 4\lambda_{\eta v})\Lambda^2S_z^2 \\ &+ 4\lambda_{\eta v}L_zS_z^3 - (A_{\eta v} - 2B_{\eta v})\Lambda^2(\boldsymbol{N}\cdot\boldsymbol{S}) - B_{\eta v}(\boldsymbol{N}^2L_zS_z + L_zS_z\boldsymbol{N}^2) \\ &- 2\lambda_{\eta v}[(\boldsymbol{N}\cdot\boldsymbol{S})L_zS_z + L_zS_z(\boldsymbol{N}\cdot\boldsymbol{S})]\}. \end{aligned} \tag{7.249}$$

The fifth term on the right-hand side has the operator form $\Lambda^2(\boldsymbol{N}\cdot\boldsymbol{S})$. Hence if s_1 is chosen as

$$s_1 = \gamma_{\eta v}/(A - 2B_{\eta v})\Lambda^2, \tag{7.250}$$

we can eliminate the term in $(\boldsymbol{N}\cdot\boldsymbol{S})$ from $\tilde{\mathcal{H}}_{\eta v}$. This choice of the transformation also modifies the coefficients of the surviving terms in $\tilde{\mathcal{H}}_{\eta v}$ as follows:

$$\tilde{A}_{\eta v} = A_{\eta v} + \gamma_{\eta v}(A_{\eta v}\Lambda^2 - 4\lambda_{\eta v}\boldsymbol{S}^2)/(A_{\eta v} - 2B_{\eta v})\Lambda^2, \tag{7.251}$$

$$\tilde{A}_{\eta Dv} = A_{\eta Dv} - 2B_{\eta v}\gamma_{\eta v}/(A_{\eta v} - 2B_{\eta v})\Lambda^2. \tag{7.252}$$

Equation (7.252) is a generalisation of (7.242). Alternatively we can choose

$$s_1 = A_{\eta Dv}/2B_{\eta v} \tag{7.253}$$

to eliminate the $A_{\eta Dv}$ term in $\tilde{\mathcal{H}}_{\eta v}$. In this case, the parameters $\tilde{A}_{\eta v}$ and $\tilde{\gamma}_{\eta v}$ are modified to:

$$\tilde{A}_{\eta v} = A_{\eta v} + A_{\eta Dv}(A_{\eta v}\Lambda^2 - 4\lambda_{\eta v}\boldsymbol{S}^2)/2B_{\eta v}, \tag{7.254}$$

$$\tilde{\gamma}_{\eta v} = \gamma_{\eta v} - A_{\eta Dv}(A_{\eta v} - 2B_{\eta v})\Lambda^2/2B_{\eta v}. \tag{7.255}$$

As well as modifying the coefficients of existing terms in $\mathcal{H}_{\eta v}$, the transformation also introduces new terms in $L_zS_z^3$ and $\{(\boldsymbol{N}\cdot\boldsymbol{S})L_zS_z + L_zS_z(\boldsymbol{N}\cdot\boldsymbol{S})\}$. For a doublet state, these terms do not arise because $\lambda_{\eta v}$ must equal zero; the elimination therefore modifies the coefficients in the Hamiltonian without altering its form. This neat property does not hold for states of higher multiplicity. However, we note that the additional contribution in $L_zS_z^3$ has essentially the same form as the higher-order spin–orbit interaction $\eta_{\eta v}$ in section 7.4.7 and so will modify that parameter if it is included. Alternatively, we could choose the form of F_1 so as to eliminate it from the transformed Hamiltonian.

Before we leave this topic, it is well to remember that we have confined our attention to the leading contribution in the transformed Hamiltonian in (7.247). If the transformation operator is not small, we may have to include higher-order effects from the second and subsequent pairs of braces in this equation. This corresponds to retention of the terms in γ^2 in equation (7.241). Furthermore, the commutator $[F, \mathcal{H}_{\eta v}^{(1)}]$ in the second brace has the potential to modify the parameters and forms of all the terms in $\mathcal{H}_{\eta v}^{(1)}$. If a particular choice is made for s_1, as say in equations (7.250) or (7.253), parameters determined in the empirical fit will also be modified. This modification must be taken into account if the parameters so obtained are to be used to provide

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structural information on the molecule. For example, some of the parameters in the Zeeman Hamiltonian, equation (7.232), are affected by the transformation given in equation (7.248). The details are presented elsewhere [34, 35].

7.8. Estimates and interpretation of parameters in the effective Hamiltonian

7.8.1. Introduction

As we explained earlier in this chapter, one of the great merits of the effective Hamiltonian is that it allows the two tasks of fitting experimental data and interpreting the resultant parameters to be separated. In this section we discuss the latter aspect and explain how the quantities obtained from a fit of experimental data can be interpreted in terms of the geometric and electronic structure of the molecule concerned. We have seen how the process of averaging the parameters over the vibrational motion of the molecule leads to additional terms which describe the vibrational dependence of the parameters. We shall assume in what follows that all such vibrational averaging effects have been properly taken into account and that we are left to deal with the equilibrium value of the parameter, P_e, in equation (7.180).

7.8.2. Rotational constant

It is well known, and shown earlier in this book, that the rotational constant of a diatomic molecule is very simply related to its bond length (R) and reduced mass (μ),

$$B_e(\mathrm{cm}^{-1}) = \hbar^2/(2\mu R_e^2 hc). \tag{7.256}$$

The dominant contribution to the rotational constant is from the nuclear masses. There is also a small contribution from the electrons in the molecule which is of the order $(m_e/m_N)B_e = \kappa^4 B_e \approx 10^{-4} B_e$, where m_e and m_N are the masses of an electron and a typical nucleus respectively and $\kappa = (m_e/m_N)^{1/4}$ is the Born–Oppenheimer expansion parameter discussed in chapter 6. Since the electrons interact strongly with the nuclei, they tend to follow their motion closely. The bulk of the electronic contribution to the moment of inertia can therefore be taken into account by the use of atomic rather than nuclear masses in the reduced mass μ in equation (7.256). However, as we have seen in section 7.4.2, equation (7.256) gives only the first-order contribution to the rotational constant. There is also a small but not insignificant second-order contribution which describes the slippage of the electronic contribution to the moment of inertia, that is, the extent to which the electrons do not follow the nuclear motion. Although this second-order contribution is large compared with the measurement errors of high resolution spectroscopy, it only reveals itself as small inconsistencies which arise when the equilibrium rotational constants of different isotopomers are compared with each other according to elementary theory (because it is proportional to μ^{-2} rather than

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μ^{-1}). In effect, the equilibrium bond lengths of different isotopomers are found to be slightly different. As we have discussed elsewhere, Watson [25] has shown that the equilibrium bond length R_e obtained by the use of equation (7.256) can be related to the Born–Oppenheimer equilibrium bond length R_e^{BO} (the bond length at the minimum of the potential energy curve) by the equation

$$R_e = R_e^{\mathrm{BO}}\left[1 + m_e\left\{\frac{d_1}{M_1} + \frac{d_2}{M_2}\right\}\right], \tag{7.257}$$

where M_1, M_2 are the masses of the atoms 1 and 2 and d_1, d_2 are dimensionless, isotopically invariant parameters. These parameters can be determined either by fitting the experimentally determined values of R_e to equation (7.257) or from theoretical estimates described by Watson. They give information on the non-adiabatic mixing effects, that is, the breakdown of the Born–Oppenheimer approximation.

7.8.3. Spin–orbit coupling constant, *A*

The spin–orbit coupling constant A is the coefficient of the operator term $L_z S_z$ in the effective Hamiltonian. It arises from the operator $\mathcal{H}_{\mathrm{so}}^{(e)}$ in equation (7.71); we have seen in section 7.4.4 how the matrix elements of this operator lead to first-, second- and higher-order contributions in the effective Hamiltonian,

$$A = A^{(1)} + A^{(2)} + \cdots. \tag{7.258}$$

If accurate electronic wave functions are available, $A^{(1)}$ and $A^{(2)}$ can be estimated from equations (7.109) and (7.120) respectively. All nearby electronic states which contribute by spin–orbit mixing to $A^{(2)}$ must be included if the result is to be reliable.

A simpler but less accurate approach to the estimation of A is often worthwhile because it provides greater physical insight. Often this estimate is just the expectation value of the microscopic operator

$$\mathcal{H}_{\mathrm{so}}^{(e)} = \sum_i a_i \mathrm{T}^1(\boldsymbol{l}_i) \cdot \mathrm{T}^1(\boldsymbol{s}_i), \tag{7.259}$$

as described in equation (7.113), using a molecular orbital approximation to the wavefunction. The summation in equation (7.259) is restricted to open shell electrons. To see why this is so, consider the spin–orbit coupling for a molecule in a $^1\Sigma^+$ state arising from the closed shell configuration π^4. As we described in section 6.5.4, the four-electron wave function for this state can be expressed as a Slater determinant

$$|\psi\rangle = (1/2\sqrt{6})\left|\pi_{+1}^{\alpha}\pi_{+1}^{\beta}\pi_{-1}^{\alpha}\pi_{-1}^{\beta}\right|. \tag{7.260}$$

The expression on the right-hand side is a convenient shorthand for a 4×4 determinant,

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listing the diagonal elements of the full determinant, which is

$$\left|\pi^{\alpha}_{+1}\pi^{\beta}_{+1}\pi^{\alpha}_{-1}\pi^{\beta}_{-1}\right| \equiv \begin{vmatrix} \pi^{\alpha}_{+1}(1) & \pi^{\beta}_{+1}(1) & \pi^{\alpha}_{-1}(1) & \pi^{\beta}_{-1}(1) \\ \pi^{\alpha}_{+1}(2) & \pi^{\beta}_{+1}(2) & \pi^{\alpha}_{-1}(2) & \pi^{\beta}_{-1}(2) \\ \pi^{\alpha}_{+1}(3) & \pi^{\beta}_{+1}(3) & \pi^{\alpha}_{-1}(3) & \pi^{\beta}_{-1}(3) \\ \pi^{\alpha}_{+1}(4) & \pi^{\beta}_{+1}(4) & \pi^{\alpha}_{-1}(4) & \pi^{\beta}_{-1}(4) \end{vmatrix} \tag{7.261}$$

The contribution to the spin–orbit energy is therefore given by

$$\begin{aligned} E_{\rm so} &= \langle\psi|\mathcal{H}^{(\rm e)}_{\rm so}|\psi\rangle = (1/2)a_1 - (1/2)a_2 - (1/2)a_3 + (1/2)a_4 \\ &= a[(1/2) - (1/2) - (1/2) + (1/2)] = 0, \end{aligned} \tag{7.262}$$

since the spin–orbit coupling constant for each electron in the *same* molecular orbital is the same.

Let us now consider a molecule which does show a spin–orbit splitting, namely, OH in its $^2\Pi$ ground state. The orbital configuration for this state is $\sigma^2\pi^3$ and confining our attention to the open shell orbital, the spin–orbital wave functions and energies for the two spin components are as follows:

$$\begin{aligned} &^2\Pi_{3/2} \quad (1/\sqrt{6})\left|\pi^{\alpha}_{+1}\pi^{\beta}_{+1}\pi^{\alpha}_{-1}\right| \quad E_{\rm so} = a[(1/2) - (1/2) - (1/2)] = -a/2, \\ &^2\Pi_{1/2} \quad (1/\sqrt{6})\left|\pi^{\alpha}_{+1}\pi^{\beta}_{+1}\pi^{\beta}_{-1}\right| \quad E_{\rm so} = a[(1/2) - (1/2) + (1/2)] = a/2. \end{aligned} \tag{7.263}$$

Thus the spin–orbit splitting is

$$\Delta E_{\rm so} = E(\Omega = 3/2) - E(\Omega = 1/2) = -a. \tag{7.264}$$

When compared with the diagonal element of the spin–orbit operator in the effective Hamiltonian, $A\Lambda\Sigma$ in a Hund's case (a) representation, we see that

$$A = -a \tag{7.265}$$

(strictly this is the value for $A^{(1)}$ in equation (7.125)). A common approximation for the molecular orbital is to represent it by a linear combination of suitable atomic orbitals. In the case of a π orbital, these atomic orbitals are p orbitals, one on each atom of the diatomic molecule:

$$|\pi\rangle = c_1|p\pi_1\rangle + c_2|p\pi_2\rangle. \tag{7.266}$$

With this approximation, the microscopic spin–orbit coupling parameter is

$$a_\pi = \langle\pi|\mathcal{H}_{\rm so}|\pi\rangle = c_1^2\zeta_1(p) + c_2^2\zeta_2(p), \tag{7.267}$$

where $\zeta_i(p)$ is the atomic spin–orbit coupling parameter for an electron in the appropriate p orbital. In other words, it is possible to relate the molecular parameter to the corresponding atomic ones. This result was first exploited by Dixon and Kroto [36]. In the case of OH, the LCAO approximation suggests that the π molecular orbital is satisfactorily described by a $2p$ orbital on the O atom. Using the value for the atomic spin–orbit coupling parameter for O of 151 cm^{-1}, we obtain a first-order estimate of the spin–orbit coupling constant of OH in its $X\,^2\Pi$ state of -151 cm^{-1}, which compares reasonably

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well with the experimental value of $-139\ \mathrm{cm}^{-1}$. The second-order contribution to the effective spin–orbit coupling parameter comes from the admixture of the first excited electronic state of OH, the $A\,^2\Sigma^+$ state, which arises from the $\sigma^1\pi^4$ configuration. Using the LCAO approximation, the matrix element of $\mathcal{H}_{\mathrm{so}}$ between these two states is

$$\left\langle {}^2\Sigma_{1/2}\middle|\mathcal{H}_{\mathrm{so}}\middle|{}^2\Pi_{1/2}\right\rangle = (a/2)\langle\lambda = 0|l_-|\lambda = 1\rangle \simeq (a/2)[l(l+1)]^{1/2} = (a/\sqrt{2}). \tag{7.268}$$

In writing this equation, we have made use of Van Vleck's *pure precession* hypothesis [12], in which the molecular orbital $|\lambda\rangle$ is approximated by an atomic orbital with well-defined values for the quantum numbers n, l and λ. Such an orbital implies a spherically symmetric potential and its use is most appropriate when the electronic distribution is nearly spherical. Examples of this situation occur quite often in the description of Rydberg states. It is also appropriate for hydrides like OH where the molecule is essentially an oxygen atom with a small pimple, the hydrogen atom, on its side. Accepting the pure precession hypothesis allows the matrix elements of the orbital operators to be evaluated since

$$l_\pm|n, l, \lambda\rangle = [l(l+1) - \lambda(\lambda \pm 1)]^{1/2}|n, l, \lambda \pm 1\rangle. \tag{7.269}$$

The second-order effect of the mixing between the $^2\Pi$ and $^2\Sigma^+$ states is

$$\Delta E_{\mathrm{so}}^{(2)} = a^2/2\lfloor E(^2\Sigma) - E(^2\Pi)\rfloor = 0.35\ \mathrm{cm}^{-1} \tag{7.270}$$

for an energy separation of $32\,600\ \mathrm{cm}^{-1}$. This interaction pushes the $^2\Pi_{1/2}$ component down and so reduces the spin–orbit splitting, that is, $A^{(2)} = 0.35\ \mathrm{cm}^{-1}$. This is a move in the right direction but not nearly large enough to improve significantly the agreement with the experimental value.

For a non-hydride molecule such as NO, we must use equation (7.267) to estimate the spin–orbit coupling parameter. NO also has a $^2\Pi$ ground state but it arises from a π^1 configuration. Estimates from the magnetic hyperfine interactions suggest that $c_{\mathrm{N}}^2 = 0.734$ and $c_{\mathrm{O}}^2 = 0.470$ [37]. From this we calculate a value for $A^{(1)}$ of $124.8\ \mathrm{cm}^{-1}$ using $\zeta_{\mathrm{O}} = 151\ \mathrm{cm}^{-1}$ and $\zeta_{\mathrm{N}} = 73.3\ \mathrm{cm}^{-1}$. The agreement with the experimentally determined value of $123.3\ \mathrm{cm}^{-1}$ is probably fortuitously good.

Finally let us consider one more example, the more complicated case of FeH in its low-lying $a^6\Delta$ state. The lowest spin component is $^6\Delta_{9/2}$ which is reasonably well approximated by the wave function

$$\left|{}^6\Delta_{9/2}\right\rangle = 1/(7!)^{1/2}\left|\delta_{+2}^{\alpha}\delta_{+2}^{\beta}\delta_{-2}^{\alpha}\pi_{+1}^{\alpha}\pi_{-1}^{\alpha}\sigma^{\alpha}\bar{\sigma}^{\alpha}\right|, \tag{7.271}$$

where the first six molecular orbitals are essentially non-bonding $3d$ orbitals on the Fe atom and the $\bar{\sigma}$ orbital is an antibonding combination of the $1s$ orbital on the H atom and an *sp* hybrid ($n = 4$) on the Fe atom. (There is also a σ^2 contribution to the electron configuration which has been omitted from equation (7.271) for the sake of simplicity. It is the bonding combination of the two atomic orbitals and is primarily responsible for holding the atoms together.) The spin–orbit energy for this wave function using the microscopic Hamiltonian is

$$E_{\mathrm{so}} = a(1 - 1 - 1 + 1/2 - 1/2 + 0 + 0) = -a. \tag{7.272}$$

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The wave function for the next spin component of the $^6\Delta$ state can be easily generated from (7.271) by application of the total spin lowering operator S_-, given by

$$S_- = \sum_{i=1}^{7} s_{i-}. \tag{7.273}$$

We obtain

$$\begin{aligned}\left|^6\Delta_{7/2}\right\rangle = (1/\sqrt{7!})(1/\sqrt{5}) \times \{&\left|\delta^\alpha_{+2}\delta^\beta_{+2}\delta^\beta_{-2}\pi^\alpha_{+1}\pi^\alpha_{-1}\sigma^\alpha\bar{\sigma}^\alpha\right| + \left|\delta^\alpha_{+2}\delta^\beta_{+2}\delta^\alpha_{-2}\pi^\beta_{+1}\pi^\alpha_{-1}\sigma^\alpha\bar{\sigma}^\alpha\right| \\ &+ \left|\delta^\alpha_{+2}\delta^\beta_{+2}\delta^\alpha_{-2}\pi^\alpha_{+1}\pi^\beta_{-1}\sigma^\alpha\bar{\sigma}^\alpha\right| + \left|\delta^\alpha_{+2}\delta^\beta_{+2}\delta^\alpha_{-2}\pi^\alpha_{+1}\pi^\alpha_{-1}\sigma^\beta\bar{\sigma}^\alpha\right| \\ &+ \left|\delta^\alpha_{+2}\delta^\beta_{+2}\delta^\alpha_{-2}\pi^\alpha_{+1}\pi^\alpha_{-1}\sigma^\alpha\bar{\sigma}^\beta\right|\}.\end{aligned} \tag{7.274}$$

For this wave function

$$E_{\rm so} = (a/5)(1 - 2 + 0 - 1 - 1) = -(3a/5). \tag{7.275}$$

The separation between adjacent spin components is therefore $-2a/5$ which equates with $2A^{(1)}$ from the effective Hamiltonian. Hence $A^{(1)} = -a/5$ or -83.4 cm^{-1}, using $\zeta_{\rm Fe} = 417$ cm^{-1}. The value obtained from experiment is -77.3 cm^{-1} although in practice it is difficult to model the spin–rotation levels of FeH with an effective Hamiltonian because of large spin–orbit perturbations [38]. For molecules like FeH, one would expect second- and higher-order contributions to A to be significant.

7.8.4. Spin–spin and spin–rotation parameters, λ and γ

A theoretical estimate of the spin–spin parameter in the effective Hamiltonian can be made by the use of equations (7.111) and (7.121) using either *ab initio* or simpler, less accurate wave functions. This was done for the case of O_2 in its $^3\Sigma_g^-$ ground state in an influential paper by Kayama and Baird [39]. They demonstrated that, in the case of a π^2 configuration (which occurs quite commonly in practice), there is significant spin–orbit mixing between the lowest $^3\Sigma^-$ state and the metastable $^1\Sigma^+$ state which arises from the same electron configuration. This has the effect of lowering the $\Omega = 0$ component of the $^3\Sigma^-$ state and so makes a positive contribution to the spin–spin parameter. For molecules with heavy atoms and large spin–orbit interactions, this becomes the dominant contribution to λ. In their paper Kayama and Baird calculate a value of 0.822 cm^{-1} for $\lambda^{(1)}$ and 0.86 cm^{-1} for $\lambda^{(2)}$ for O_2, giving a total value for λ of 1.682 cm^{-1} (to be compared with the experimental value of 1.985 cm^{-1}). A later calculation by Wayne and Colbourne [40] gave $\lambda^{(1)} = 0.750$ cm^{-1}.

The way in which the second-order contribution arises can be appreciated from the following. The spin–orbital wave functions for the $^3\Sigma_0^-$ and $^1\Sigma_0^+$ states are approximated by

$$\begin{aligned}\left|^3\Sigma_0^-\right\rangle &= (1/\sqrt{2})\{\left|\pi^\alpha_{+1}\pi^\beta_{-1}\right| + \left|\pi^\beta_{+1}\pi^\alpha_{-1}\right|\}, \\ \left|^1\Sigma_0^+\right\rangle &= (1/\sqrt{2})\{\left|\pi^\alpha_{+1}\pi^\beta_{-1}\right| - \left|\pi^\beta_{+1}\pi^\alpha_{-1}\right|\}.\end{aligned} \tag{7.276}$$

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Hence the spin–orbit matrix element is given by

$$\left\langle {}^3\Sigma_0^- \left| \mathcal{H}_{\rm so} \right| {}^1\Sigma_0^+ \right\rangle = (a/2)\{(1/2+1/2) - (-1/2-1/2)\} = a. \tag{7.277}$$

In addition equation (7.267) tells us that for a homonuclear diatomic molecule, $a = \zeta$. Consequently

$$\lambda^{(2)} = -(1/2)\left\langle {}^3\Sigma_0^- \left| \mathcal{H}_{\rm so} \right| {}^1\Sigma_0^+ \right\rangle^2 \Big/ \left\{ E\left({}^3\Sigma_0\right) - E\left({}^1\Sigma_0\right) \right\}. \tag{7.278}$$

Using $\zeta_{\rm O} = 151\ {\rm cm}^{-1}$ and a value of $-13\ 120\ {\rm cm}^{-1}$ for the energy denominator, we obtain a value of $0.864\ {\rm cm}^{-1}$ for $\lambda^{(2)}$.

A very similar treatment can be applied to the spin–rotation parameter γ. Once again there is a first- and second-order contribution with the second-order contribution dominating in all but the lightest molecules. Full expressions for $\gamma^{(1)}$ and $\gamma^{(2)}$ are given in equations (7.110) and (7.122).

Semi-empirical estimates of the second-order contribution to γ provide a useful means to interpret experimental data. Reverting to the case of OH in its $X\,^2\Pi$ state, we need the matrix elements

$$\left\langle {}^2\Pi_{1/2} \left| \mathcal{H}_{\rm so} \right| {}^2\Sigma_{1/2}^+ \right\rangle = a/\sqrt{2}, \tag{7.279}$$

$$\begin{aligned} \left\langle {}^2\Sigma_{1/2} \right| - BL_- \left| {}^2\Pi_{3/2} \right\rangle &= (1/5!)\left\langle \left| \sigma^\alpha \pi_{+1}^\alpha \pi_{+1}^\beta \pi_{-1}^\alpha \pi_{-1}^\beta \right| \right| - BL_- \left| \left| \sigma^\alpha \sigma^\beta \pi_{+1}^\alpha \pi_{+1}^\beta \pi_{-1}^\alpha \right| \right\rangle \\ &= \langle \lambda = -1 | Bl_- | \lambda = 0 \rangle \cong \sqrt{2}B. \end{aligned} \tag{7.280}$$

The first result has been obtained earlier; in obtaining the second result, we have to take account of the sign change which results from the permutation of the order of the orbitals (required to set up the one-electron result). We have also used the pure precession hypothesis to evaluate the orbital matrix element. Using $a = 151\ {\rm cm}^{-1}$, $B = 18.535\ {\rm cm}^{-1}$ and $\{E(^2\Pi) - E(^2\Sigma^+)\} = -32\,600\ {\rm cm}^{-1}$, we obtain a value of $-0.172\ {\rm cm}^{-1}$ for $\gamma^{(2)}$ for OH in the $X\,^2\Pi$ state, somewhat larger in magnitude than the experimental value of $-0.119\ {\rm cm}^{-1}$. More accurate calculations using *ab initio* wave functions suggest that it is mainly the estimate of the off-diagonal element of $\mathcal{H}_{\rm so}$ in equation (7.279) which is too large [41]. The *ab initio* value for this matrix element corresponds to a value for a of $111.7\ {\rm cm}^{-1}$ which gives much better agreement with the experimental value.

Before we leave OH, it is instructive to use the same semi-empirical model to estimate the value of $\gamma^{(2)}$ for the $A\,^2\Sigma^+$ state. In this case, we find that the combined effect of spin–orbit and rotational coupling with the $X\,^2\Pi$ state gives a value for $\gamma^{(2)}$ which has the opposite sign (because of the change in sign of the energy denominator) and which is twice as big, that is, $0.344\ {\rm cm}^{-1}$. The latter difference occurs because the $|\Lambda = 0\rangle$ orbital of the $^2\Sigma^+$ state interacts with both $|\Lambda = +1\rangle$ and $|\Lambda = -1\rangle$ components of the $^2\Pi$ state. The experimental value of γ for OH in the $A^2\Sigma^+$ state is $0.201\ {\rm cm}^{-1}$.

By this stage, it will be apparent that even the sign of the spin–rotation parameter contains valuable information on the electronic structure of the molecule. To appreciate this point fully, let us consider a $^3\Sigma$ state which arises from a $\pi^{\ 2}$ electron configuration. The effective spin–rotation interaction arises from second-order mixing with $^3\Pi$ states. Let us assume that there is only one such state which lies higher in energy so that the

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energy denominator $\{E(^3\Sigma) - E(^3\Pi)\}$ in equation (7.122) is negative. If the $^3\Pi$ state is obtained by promotion of an electron from an inner σ orbital ($\sigma^2\pi^2 \rightarrow \sigma^1\pi^3$), the matrix elements involved in the calculation of $\gamma^{(2)}$ are of the form

$$\begin{aligned}\left\langle {}^3\Pi_1 \middle| -BL_+ \middle| {}^3\Sigma_0 \right\rangle &= \left\langle \left|\sigma^\beta \pi^\alpha_{+1}\pi^\beta_{+1}\pi^\alpha_{-1}\right| \right| -BL_+ \left|\left|\sigma^\alpha\sigma^\beta\pi^\beta_{+1}\pi^\alpha_{-1}\right|\right\rangle,\\ \left\langle {}^3\Pi_1 \middle| \mathcal{H}_{\rm so} \middle| {}^3\Sigma_1 \right\rangle &= \left\langle \left|\sigma^\beta \pi^\alpha_{+1}\pi^\beta_{+1}\pi^\alpha_{-1}\right| \right| \mathcal{H}_{\rm so} \left|\left|\sigma^\alpha\sigma^\beta\pi^\alpha_{+1}\pi^\alpha_{-1}\right|\right\rangle. \end{aligned} \tag{7.281}$$

Permutation of the order of the molecular orbitals in the Slater determinant to reduce them to one-electron integrals shows that both these matrix elements are positive and so their product is also positive. Consequently, $\gamma^{(2)}$ is negative for this particular electronic excitation. By contrast, when we investigate mixing by a $^3\Pi$ state obtained by promotion of a π electron to an outer σ orbital ($\pi^2 \rightarrow \pi\sigma$), the corresponding matrix elements are:

$$\begin{aligned}\left\langle {}^3\Pi_1 \middle| -BL_+ \middle| {}^3\Sigma_0 \right\rangle &= \left\langle \left|\pi^\alpha_{+1}\sigma^\beta\right| \right| -BL_+ \left|\left|\pi^\alpha_{+1}\pi^\beta_{-1}\right|\right\rangle,\\ \langle {}^3\Pi_1 |\mathcal{H}_{\rm so}| {}^3\Sigma_1 \rangle &= \left\langle \left|\pi^\alpha_{+1}\sigma^\beta\right| \right| \mathcal{H}_{\rm so} \left|\left|\pi^\alpha_{+1}\pi^\alpha_{-1}\right|\right\rangle. \end{aligned} \tag{7.282}$$

The rotational kinetic energy matrix element is now negative while that of the spin–orbit coupling remains positive. In this case, therefore, $\gamma^{(2)}$ is positive.

7.8.5. Λ-doubling parameters

As we have seen in section 7.4.5, the Λ-doubling parameters in the effective Hamiltonian, like the spin–spin and spin–rotation parameters, arise from the mixing of electronic states by the spin–orbit interaction and rotational coupling. However, Λ-doubling effects must involve a non-degenerate Σ electronic state at some stage whereas the spin–spin and spin–rotation couplings do not have to do so. For a molecule in a Π state, Λ-doubling arises through second order mixing with a remote Σ state. For a molecule in a Δ state, on the other hand, Λ-doubling arises from fourth-order mixing with a remote Σ state through an intermediate Π state. For this reason, Λ-doubling effects are smaller for molecules in Δ states than for those in Π states. The other important feature of the Λ-doubling parameters is that, with the exception of the parameter o, they do not have a first-order contribution in the effective Hamiltonian. The leading contribution is the second-order one described in section 7.4.5 for molecules in Π electronic states.

For OH in its $X^2\Pi$ state, there are two Λ-doubling parameters, p and q. Using the explicit expressions given in equations (7.142) and (7.143), these parameters can be calculated very accurately using good quality *ab initio* wave functions. A simple estimate can be made using the pure precession values for the relevant matrix elements which we have derived earlier. This approximation assumes that the Λ-doubling effects arise wholly from the perturbations with the $A^2\Sigma^+$ state. For this approximation,

$$p = -4B\zeta/\{E(\Pi) - E(\Sigma^+)\} = 0.3434\,\text{cm}^{-1}, \quad cf.\text{expt}, 0.2503\,\text{cm}^{-1}, \tag{7.283}$$

$$q = 4B^2/\{E(\Pi) - E(\Sigma^+)\} = -0.0422\,\text{cm}^{-1}, \quad cf.\text{expt}, -0.0387\,\text{cm}^{-1}. \tag{7.284}$$

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Once again, we see that the values of these two parameters are reasonably well reproduced by this very simple calculation.

Later on in this book, we discuss the properties of the CH radical in its $X^2\Pi$ state in some detail. The electronic structure of this radical is rather more complicated than that of OH. Despite this, a simple pure precession calculation of the Λ-doubling parameters reproduces the experimental values (particularly q) reasonably well (see section 10.6.3).

7.8.6. Magnetic hyperfine interactions

Nuclear hyperfine interactions may be small in magnitude but it would be wrong to dismiss them as insignificant. Indeed, they provide highly specific and accurate information on the electronic wave function. This is because the interactions fall off very rapidly with distance from the nucleus (typically as the inverse cube of the separation of the electron from the nucleus although the Fermi contact interaction provides information of the electron density only at the nucleus). In addition, the magnetic hyperfine interactions depend on the open shell electrons only. As with the other interactions, the effective Hamiltonian provides explicit formulae for the calculation of the hyperfine parameters (see, for example, equations (7.154), (7.156) and (7.162)). Because of the small size of these interactions, it is usually only the first-order contribution which is significant. It is therefore relatively easy to calculate their values using *ab initio* wave functions.

If we confine attention to molecules in a $^{2S+1}\Pi$ electronic state, there are four magnetic hyperfine parameters, a, b_F, c and d. The first of these describes the strength of the nuclear-spin/electron–orbital interaction and gives information on the spatial distribution of the unpaired electrons. The other three parameters give information on the electron spin distribution within the molecule. Though often similar, these two distribution functions are not identical.

A complete characterisation of the magnetic hyperfine parameters has been achieved for several free radicals in $^2\Pi$ electronic states. One such example is the CF radical which is isoelectronic with NO. The values of the four hyperfine parameters for the ^{19}F nucleus ($I = 1/2$) are given in table 7.3 together with the expectation values of the corresponding distribution functions over the electronic wave function. It can be seen that the hyperfine parameter a is related to the orbital distribution $\langle r^{-3}\rangle_l$ where r is the distance between the unpaired electron and the F nucleus, the Fermi contact parameter b_F is a measure of the spin density at the nucleus $|\Psi(0)|^2$, whilst c and d are associated with the angular spin distributions $\langle(3\cos^2\theta - 1)/r^3\rangle_s$ and $\langle\sin^2\theta/r^3\rangle_s$ respectively, where θ is the polar angle between the vector $\boldsymbol{r}$ and the internuclear axis. The value for $\langle r^{-3}\rangle_l$ can be compared with the corresponding value for the fluorine atom in its ground ^{2}P state (4.96×10^{31} m^{-3} [42]), suggesting that the square of the atomic orbital coefficient c_1 in equation (7.266) is 0.192. The corresponding spin average can be calculated from the sum $(d + c/3)$; the value obtained is 9.075×10^{30} m^{-3}, close to but different from that for $\langle r^{-3}\rangle_l$. The angular distribution of the

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Table 7.3. ^{19}F *hyperfine structure parameters [43] and expectation values of distribution functions over the electronic wave function of CF in its* $X\,^2\Pi$ *state*

hyperfine parameter	experimental value	function	value /m^{-3}
a	705.94 (14)	$\langle r^{-3}\rangle_l$	9.502×10^{30}
b_F	151.19 (49)	$\lvert\Psi(0)\rvert^2$	2.429×10^{30}
c	−351.6 (14)	$\langle(3\cos^2\theta - 1)/r^3\rangle_s$	-3.151×10^{30}
d	792.195 (98)	$\langle\sin^2\theta/r^3\rangle_s$	7.100×10^{30}

spin density is well modelled by a p_π orbital. For such an orbital,

$$\langle\pi|\sin^2\theta|\pi\rangle = 4/5, \tag{7.285}$$

$$\langle\pi|(3\cos^2\theta - 1)|\pi\rangle = -2/5. \tag{7.286}$$

In this approximation, the ratios $\langle r^{-3}\rangle_s : \langle(3\cos^2\theta - 1)/r^3\rangle_s : \langle\sin^2\theta/r^3\rangle_s$ are $1 : -0.4 : 0.8$, to be compared with the actual values for CF from table 7.3 of $1 : -0.35 : 0.78$.

A striking example of the specific information carried in the hyperfine parameters is provided by a study of the molecule CuO in its so-called $A'^2\Sigma^-$ state [44]. This molecule shows a large magnetic hyperfine splitting from the ^{63}Cu nucleus ($I = 3/2$), so large in fact that it can be resolved in the Doppler-limited optical spectrum associated with the $A'^2\Sigma^- – X^2\Pi$ transition. The hyperfine structure can be interpreted in terms of a large Fermi contact interaction and a fit of the data to the effective Hamiltonian for a $^2\Sigma^s$ state gives a value of –0.052 (22) cm^{-1} for the parameter b_F. We note that this value is both large and *negative*. The sign, in particular, cannot be explained by the simplistic definition of the Fermi contact parameter,

$$b_F = (2g_S\mu_B g_N\mu_N\mu_0/3)|\Psi(0)|^2, \tag{7.287}$$

where all the terms on the right-hand side are positive. The proper explanation provides insight into the nature of the electronic wave function. The likely configuration for the A' state is $\ldots 1\delta^4 9\sigma^2 4\pi^2 10\sigma$ where the 1δ orbital is essentially localised on the Cu atom, the 9σ and 4π orbitals are predominantly O $2p$ atomic orbitals and the 10σ orbital is a $4s$ orbital localised on the metal atom. The states which arise from this configuration are $^2\Sigma^+$, $^2\Sigma^-$, $^2\Delta_r$ and $^4\Sigma^-$. The spin–orbital wave functions for the $^2\Sigma^+$ and $^2\Sigma^-$ states are [45]

$$|^2\Sigma^+\rangle = (2)^{-1/2}(6)^{-1/2}\left\{\left|4\pi^\beta_{+1}4\pi^\alpha_{-1}10\sigma^\alpha\right| - \left|4\pi^\alpha_{+1}4\pi^\beta_{-1}10\sigma^\alpha\right|\right\}, \tag{7.288}$$

$$|^2\Sigma^-\rangle = (6)^{-1}\left\{2\left|4\pi^\alpha_{+1}4\pi^\alpha_{-1}10\sigma^\beta\right| - \left|4\pi^\beta_{+1}4\pi^\alpha_{-1}10\sigma^\alpha\right| - \left|4\pi^\alpha_{+1}4\pi^\beta_{-1}10\sigma^\alpha\right|\right\}. \tag{7.289}$$

Using the full form of the Fermi contact hyperfine interaction given in equation (7.144), which differs from equation (7.287) in that it contains an explicit summation over the open shell electrons, we have that

$$\langle^2\Sigma^+|\delta(\boldsymbol{r})s_z|^2\Sigma^+\rangle = (1/2)|\Psi_{10\sigma}(0)|^2, \tag{7.290}$$

$$\langle^2\Sigma^-|\delta(\boldsymbol{r})s_z|^2\Sigma^-\rangle = -(1/6)|\Psi_{10\sigma}(0)|^2. \tag{7.291}$$

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where $\delta(\boldsymbol{r})$ and s_z act on the 10σ electron only. A value for $|\Psi_{10\sigma}(0)|^2$ can be obtained from the optical spectrum of the Cu atom which, in its ground state, has one unpaired electron in a $4s$ orbital which produces a Fermi contact parameter of 0.0967 cm^{-1}. Using this value, we can make the following estimates,

$$b_{\mathrm{F}}(^2\Sigma^+) = 0.0967\,\mathrm{cm}^{-1}, \tag{7.292}$$

$$b_{\mathrm{F}}(^2\Sigma^-) = -0.0322\,\mathrm{cm}^{-1}. \tag{7.293}$$

The experimental value for b_{F} clearly supports the assignment of the A' state as $^2\Sigma^-$. The value for the $^2\Sigma^-$ state is negative because the contribution of the β spin in the $\sigma(4s)$ orbital in equation (7.289) outweighs that for the α spins.

We see that the analysis of the hyperfine structure in this case provides a simple and direct way of distinguishing between Σ^+ and Σ^- states. It depends on the precise form of the electron spin part of the total molecular wave function which is permitted by the Pauli exclusion principle. It has the advantage that it does not require a knowledge of the parities of the individual states. This contrasts with the traditional way of making the Σ^+/Σ^- assignment which is based on a consideration of the orbital part of the wave function.

7.8.7. Electric quadrupole hyperfine interaction

The form of the nuclear electric quadrupole interaction in the effective Hamiltonian for a diatomic molecule is given in equations (7.158) and (7.161), with the latter applying only to molecules in Π electronic states. The two parameters which can be determined from a fit of the experimental data are eq_0Q and eq_2Q respectively. Since the electric quadrupole moment eQ is known for most nuclei, an experimental observation gives information on q_0 (and perhaps q_2), the electric field gradient at the nucleus. This quantity depends on the electronic structure of the molecule according to the expression

$$\begin{aligned} q_0 &= -2\langle \eta, \Lambda | \mathrm{T}^2_{q=0}(\nabla \boldsymbol{E}) | \eta, \Lambda \rangle \\ &= \langle \eta, \Lambda | \partial^2 V / \partial z^2 | \eta, \Lambda \rangle, \end{aligned} \tag{7.294}$$

and is strictly the negative of the electric field gradient.

Let us consider a nucleus with $I \geq 1$ in atom 1 of a diatomic molecule. We shall use a local coordinate system (x, y, z) with its origin at the nucleus and z lying along the molecular bond. An unscreened electric charge q at a distance r from the nucleus gives rise to an electrostatic potential

$$V = q/4\pi\varepsilon_0 r \tag{7.295}$$

at the nucleus. The negative of the electric field gradient at the nucleus is therefore

$$q_0 \equiv \frac{\partial^2 V}{\partial z^2} = \frac{q}{4\pi\varepsilon_0}\frac{\partial^2}{\partial z^2}[x^2 + y^2 + z^2]^{-1/2} = q\frac{(3\cos^2\theta - 1)}{4\pi\varepsilon_0 r^3}, \tag{7.296}$$

where θ is the polar angle between $\boldsymbol{r}$ and the z axis. If, as is most likely, the charged

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particle is an electron, its contribution to the electric field gradient at the nucleus may be obtained by averaging the quantity in equation (7.296) over the molecular orbital ϕ_i of the electron,

$$q_{0,i} = -\frac{e}{4\pi\varepsilon_0}\langle\phi_i|(3\cos^2\theta_i - 1)/r_i^3|\phi_i\rangle. \tag{7.297}$$

The total electric field gradient at the nucleus due to all the electrons in the molecule is therefore

$$q_0 = -\frac{e}{4\pi\varepsilon_0}\sum_i n_i\langle\phi_i|(3\cos^2\theta_i - 1)/r_i^3|\phi_i\rangle \tag{7.298}$$

where n_i (=0, 1 or 2) is the number of electrons in the ith orbital.

This discussion shows that the most accurate interpretation of the electric quadrupole coupling constant is obtained by evaluating

$$q_0 = -\frac{e}{4\pi\varepsilon_0}\langle\eta, \Lambda|\sum_i \frac{(3\cos^2\theta_i - 1)}{r^3}|\eta, \Lambda\rangle + \frac{Z_{\alpha'}e}{4\pi\varepsilon_0}\langle\eta, \Lambda|\frac{2}{R^3}|\eta, \Lambda\rangle, \tag{7.299}$$

where $|\eta, \Lambda\rangle$ is the *ab initio* electronic wave function and i is the sum over *all* electrons. The second term on the right-hand side is the contribution to the electric field gradient from the charge on the other nucleus ($\alpha' = 2$) in the diatomic molecule. Because of the R^{-3} dependence, this contribution is small. It is not, however, negligible in the most accurate calculations; for example, it makes a large (81%) contribution to the quadrupole coupling constant for ^{17}OH in its ground $^2\Pi$ state because the electronic contribution is accidentally very small in this case [46]. In addition, equation (7.299) shows that, unlike the magnetic hyperfine interactions, the electric quadrupole interaction depends on all the electrons in the molecule, which makes its calculation more arduous.

Short of the *ab initio* calculations, there are several semi-empirical approaches to the calculation and interpretation of electric quadrupole coupling constants. These were developed originally by Townes and Dailey [47, 48] and are well documented in the book by Gordy and Cook [49]. They are based on the linear combination of atomic orbitals approximation for molecular orbitals, mentioned earlier in equation (7.266) and described in more detail in chapter 6:

$$|\eta, \Lambda\rangle \simeq c_1|n_1, l_1, \lambda_1\rangle + c_2|n_2, l_2, \lambda_2\rangle. \tag{7.300}$$

This allows the local electron distribution to be modelled by atomic orbitals. The symmetry of these orbitals leads to a number of useful simplifications. First, the spherically symmetric charge distribution of s orbitals produce zero average field at the central nucleus and so do not contribute to q_0. The same remark applies to electrons in the inner closed shells of an atom, if we ignore the polarisation effects of electrons in valence shells. Furthermore, electrons in orbitals with $l = 2$ (d orbitals) or greater produce a much smaller electric field gradient at the nucleus than those in $l = 1$ (p orbitals). Finally, the contributions to q_0 of the electrons and nuclear charge of the *other* atom approximately cancel and so can be neglected. The conclusion of these simplifications is that the electric field gradient at the nucleus can be calculated by restricting attention

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to the p electrons in the valence shells of the atom in question, since these electrons make the predominant contribution to q_0. The resultant expression for the electric field gradient at nucleus 1 is thus

$$q_0 = \sum_i n_i c_i^2 q_i \tag{7.301}$$

where q_i is defined by equation (7.297) and the summation is over valence electrons in p orbitals only. This model produces reasonably reliable values for q_0 but, more importantly, it allows trends in a series of molecules to be rationalised.

In addition to the main axial component eq_0Q of the electric quadrupole interaction, there is also a perpendicular component eq_2Q for molecules in Π electronic states. Recalling that

$$\mathrm{T}^2_{\pm 2}(\nabla \boldsymbol{E}) = -\frac{1}{2\sqrt{6}}\left[\frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2}\right], \tag{7.302}$$

we see that this component measures the asymmetry of the electric field gradient perpendicular to the z axis. The particular component of the electric field gradient is given by

$$\begin{aligned} q_2 &= -2\sqrt{6}\langle \eta, \Lambda = \pm 1|\mathrm{T}^2_{\pm 2}(\nabla \boldsymbol{E})|\eta, \Lambda = \mp 1\rangle \\ &= \frac{3e}{4\pi\varepsilon_0}\langle \eta, \Lambda = \pm 1|\sum_i (\sin^2\theta_i/r_i^3)|\eta, \Lambda = \pm 1\rangle. \end{aligned} \tag{7.303}$$

Because this term is a measure of the deviation from cylindrical symmetry, there is no contribution from the charge on the other nucleus nor, to a good approximation, from the electrons in closed shell orbitals. The magnetic hyperfine parameter d also depends on the deviation of the electronic distribution from cylindrical symmetry, in this case on the non-cylindrical distribution of electron spin for a molecule in a Π electronic state. The two parameters are therefore related since they give independent estimates of the expectation values of $\langle \sin^2\theta/r^3\rangle$. For example, the following values for the two parameters have been measured for ^{35}ClO in its $^2\Pi$ state [50]:

$$d = 173.030(20)\,\mathrm{MHz}, \quad eq_2Q = -116.0(56)\,\mathrm{MHz}.$$

These correspond to expectation values

$$\langle \sin^2\theta/r^3\rangle_S = 14.88 \times 10^{30}\,\mathrm{m}^{-3}, \quad \langle \sin^2\theta/r^3\rangle_l = -14.06 \times 10^{30}\,\mathrm{m}^{-3},$$

which are similar in magnitude. The negative sign for the quadrupole coupling constant arises because the ground state of ClO is derived from a π^3 configuration. The electric field gradient at the nucleus is therefore caused by a hole in the π orbital, that is, by an effective distribution of positive charge rather than negative.

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Appendix 7.1. Molecular parameters or constants

We present below a summary of the molecular parameters which appear in effective Hamiltonians. Often the appropriate vibrational level is indicated by the subscript v and, more rarely, other vibronic quantum numbers, particularly electronic, are indicated by the subscript η. These molecular parameters are combined with operator expressions, given in the equations referenced below.

A or A_v – fine structure or molecular spin–orbit coupling constant for vibration level v. Equation (7.187).

A_D or A_{Dv} – centrifugal distortion correction to the spin–orbit coupling constant. Equation (7.187).

B or B_v – rotational constant for vibrational level v. The subscript v is often omitted when only the ground vibrational level is involved. Equation (7.185).

D or D_v – first centrifugal distortion constant. Equation (7.186).

H or H_v – second centrifugal distortion constant. Equation (7.186).

λ_v – electron spin–spin constant in vibrational level v. Equation (7.188).

λ_{Dv} – centrifugal distortion correction to the spin–spin constant. Equation (7.188).

γ_v – electron spin–rotation constant in vibrational level v. Equation (7.189).

γ_{Dv} – centrifugal distortion correction to the electron spin–rotation constant. Equation (7.189).

$C_v^{(3)}$, η_v, Θ_v – higher-order fine structure constants. Equation (7.193).

o_v, p_v, q_v – Λ-doubling parameters for Π electronic states. Equation (7.190).

o_{Dv}, p_{Dv}, q_{Dv} – centrifugal distortion corrections to the Λ-doubling constants. Equation (7.190).

a or a_v or a_v^α – electron orbital magnetic hyperfine constant. Equation (7.191).

b_F or b_{Fv} or b_{Fv}^α – Fermi contact hyperfine constant. Equation (7.191).

t_0, t_{0v}, or c_v – axial component of the electron–nuclear dipolar interaction.

c_I – nuclear spin–rotation constant.

d or t_2 – nuclear spin–electron spin dipolar interaction constant for molecules in Π electronic states.

q_0 – axial component of (the negative of) the electric field gradient. Equation (7.192).

eq_0Q – axial nuclear quadrupole coupling constant. Equation (7.192).

q_2 – perpendicular component of the electric field gradient. Equation (7.303).

g_S – electron spin g-factor with value 2 in the Dirac theory, and 2.002 319 with quantum electrodynamical correction. Equation (7.232). See also reference [32].

g_L – electron orbital g-factor with value 1. In some instances admixture of other electronic states is indicated by the alternative symbol g'_L with a value slightly different from 1. Equation (7.232). See also reference [32].

g_r – rotational g-factor. Equation (7.232).

g_l – anisotropic correction to the electron spin Zeeman interaction. Equation (7.232).

g_N or g_N^α – nuclear g -factor for nucleus α. Equation (7.232).

χ – anisotropic magnetic susceptibility constant. Equation (7.232).

σ $(\boldsymbol{J})$ – nuclear screening constant.

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